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PRODUCTION OF SULPHATE BY-PRODUCT FROM MINING WATER CONCENTRATE USING EUTECTIC FREEZE CRYSTALLISATION

Master´s Programme in Chemical, Biochemical and Materials Engineering
Major in Chemistry

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Abstract of master's thesis

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Abstract

Large volumes of affected water are a common problem in mining. Water is used in many ways in mining processes, especially in hydrometallurgy, where it is used to mainly extract and transport dissolved metals. The saline water often cannot be discharged without purification due to environmental effects and regulations. A common solution for water recovery is reverse osmosis (RO), which uses pressure and a semi-permeable membrane to desalinate water. The products are dilute solution and saline concentrate. Applying crystallisation methods to treat the concentrate would enable the production of by-product sulphate salts, which have commercial potential. An uncommon but potentially effective crystallisation method is eutectic freeze crystallisation (EFC). The method is based on cooling a saline solution to a salt's eutectic point, where equilibrium between solid salt, ice and liquid solution exists. EFC is capable of simultaneous production of highly pure salt and ice, with a very high potential water recovery. Another advantage is low energy requirement compared to evaporation. High investment costs have limited industrial use of EFC.

This study explored the application of EFC in treating concentrated mine wastewater for sulphate products. The initial experiments studied the individual crystallisations of Na_2SO_4, K_2SO_4 and $MgSO_4$ from water. The later experiments focused on crystallising K_2SO_4 from synthetic solutions with impurities and Na_2SO_4 from actual mine concentrate. Analysis was carried out by spectrophotometry, ICP-OES and manual thermogravimetric moisture analysis. Eutectic properties of the sulphates were found to be similar to literature data, with minor divergence attributed to cooling equipment. EFC of K_2SO_4 and $Na_2SO_4*10H_2O$ from mine water was found highly selective and technically suitable. Ice scaling was found to be the main drawback of EFC tests, but manual removal of ice proved to be sufficiently effective. Economical evaluation was done for a Na-based mine concentrate and a hypothetical K-based high concentration feed. The K-based feed was found to be clearly profitable for EFC treatment. The main reasons were higher sulphate market value and feed concentration. Capital cost evaluation suggests a payback period of around two years, with some resistance to cost fluctuation due to relatively low estimated operational expenses. For future study, an in-depth cost analysis for a realistic large-scale EFC process is recommended.

Keywords eutectic freeze crystallisation, reverse osmosis, mining, sulphate

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Tiivistelmä

Suuret vesimäärät ovat yleinen ongelma kaivostoiminnassa. Vettä käytetään kaivosprosesseissa monilla tavoilla, erityisesti hydrometallurgiassa, jossa sitä käytetään pääosin liuenneiden metallien talteenotossa ja kuljetuksessa. Suoloja sisältävää vettä ei voida suoraan laskea pois ilman puhdistusta ympäristövaikutusten ja -säädösten takia. Yleinen vedenpuhdistusratkaisu on käänteisosmoosi, joka puhdistaa vedestä suoloja paineen ja puoliläpäisevän kalvon avulla. Tuotteina ovat tehokkaasti laimennettu liuos ja konsentraattiliuos. Konsentraatin käsittely kiteytysmenetelmillä mahdollistaisi sulfaattien valmistuksen kaupallisina sivutuotteina. Eutektinen jäädytyskiteytys (EFC) on vähän käytetty mutta mahdollisesti tehokas kiteytysmenetelmä. Menetelmä perustuu suolaliuoksen jäähdyttämiseen sen eutektiseen pisteeseen, jossa on tasapainotila liuoksen, kiinteän suolan ja jään välillä. EFC pystyy hyvin puhtaan suolan ja jään samanaikaiseen valmistukseen, mahdollistaen korkean puhtaan veden talteenotto-osuuden. Lisäetuna on matala energiankulutus haihdutuskiteytykseen verrattuna. Suuret investointikulut ovat toistaiseksi rajoittaneet EFC:n teollista käyttöä.

Tässä työssä tutkittiin EFC:n käyttöä sulfaattituotteiden valmistukseen kaivosvesikonsentraatista. Ensimmäisissä kokeissa tutkittiin suolojen Na_2SO_4, K_2SO_4 ja $MgSO_4$ kiteytymistä yhden suolan liuoksista. Myöhemmät kokeet keskittyivät K_2SO_4:n kiteyttämiseen synteettisistä epäpuhtauksia sisältävistä liuoksista ja Na_2SO_4:n kiteyttämiseen todellisesta kaivosvesikonsentraatista. Analyysimenetelminä olivat spektrofotometria, ICP-OES ja käsin tehty termogravimetrinen kuiva-ainemääritys. Sulfaattien eutektiset ominaisuudet todettiin olevan kirjallisuusarvoja vastaavia, ja pienet erot arvioitiin liittyvän jäähdytyslaitteistoon. K_2SO_4:n ja Na_2SO_4:n kiteytys kaivosvedestä todettiin olevan hyvin selektiivistä ja teknisesti soveltuvaa. Jään kertyminen lämmönsiirtopinnoille todettiin olevan EFC-kokeiden pääheikkous, mutta jään poisto onnistui manuaalisesti. Taloudellisen arvion perusteella kaivosvesikonsentraattia väkevämpi K-pitoinen syöte olisi kaupallisesti kannattavaa K_2SO_4:n valmistamiseksi EFC-käsittelyllä. Pääomakulujen arvio viittasi takaisinmaksuajan vastaavalle prosessille olevan noin kaksi vuotta. Tuloksella vaikutti olevan liikkumavaraa kustannusvaihtelun suhteen suhteellisen matalien käyttökulujen takia. Tulevaisuuden tutkimuksille ehdotettiin syvempää kustannusanalyysiä todenmukaiselle, suurikokoiselle EFC-prosessille.

Avainsanat eutektinen jäädytyskiteytys, käänteisosmoosi, kaivostoiminta, sulfaatti

Preface

This thesis was carried out at VTT Technical Research Centre of Finland in Jyväskylä. I would like to thank Terrafame Group for the opportunity to study an uncommon and challenging technology. I learned much from working with limited existing knowledge and constantly adapting to challenges in its application. I would also like to thank Professor Sakari Kulmala for supervising this interesting project and my advisor Kaisa Kiipula for steady, critical feedback.

I wish to thank the resourceful and helpful staff of VTT Jyväskylä for their immeasurable assistance on this project. I would like to thank Eliisa Järvelä and Hanna Kyllönen for their feedback on the planning and writing of the thesis. I also wish to thank Jorma Ihalainen, Hannu Mursunen and everyone else in chemical process technologies team for their technical expertise. The crystalliser would have not been the same without you. Finally, I would like to thank Labtium for their swift and clear analyses of my samples.

Helsinki, 8.9.2017

Henri Hauensuo

Contents

Abbreviations

RO	Reverse Osmosis
EFC	Eutectic Freeze Crystallisation
PLS	Pregnant Leach Solution
EC	Evaporative Crystallisation
CDCC	Cooling Disk Column Crystalliser
FBHE	Fluidised Bed Heat Exchanger
ICP-OES	Inductively Coupled Plasma Optical Emission Spectrometry
COP	Coefficient Of Performance

1 Introduction

Treating effluent water in mining has become an increasingly important subject. Water is a major part of many mining processes, where it is used in areas such as ore processing, mineral transport and washing (Kemp, et al., 2010). Large affected water volumes present a problem to many mines, as it cannot be released into the immediate environment. Cases of environmental damage from mining spillages and water management issues have created a continuing demand for water purification (Banks, et al., 1997). Much of the water can be purified and recycled with proven methods (Lee, et al., 2016), but a saline mining water concentrate is often left behind. However, the brine contains a business opportunity for mines: extraction of commercially viable side product salts.

A common and effective choice for water recovery is reverse osmosis (RO), which uses pressure to drive water through a semipermeable membrane. In mining, the method has seen water recovery rates up to 60 % (Kyllönen, et al., 2016). Higher recovery often becomes difficult due to salt scaling and rising osmotic pressure. Due to these limits, large processes create significant amounts of hypersaline brine in addition to pure water. Treating the brine is therefore necessary for mine water management, which can be done with crystallisation methods to extract salts. Common crystallisation methods such as evaporation offer possible solutions, but complex saline brines can be difficult to treat when substances need selective extraction, and energy costs can be high for industrial uses (Randall, et al., 2011).

A potentially efficient option for salt production is eutectic freeze crystallisation (EFC). The method can be used to simultaneously separate ice and salt as high-purity solids from solutions with varying concentrations. Compared to more traditional crystallisation methods such as evaporation,

EFC is theoretically much more energy efficient, even more so in colder northern climates where outdoor evaporation is unfeasible (Fernandéz-Torres, et al., 2012). In addition, product purity is potentially very high since solution components can be crystallised individually. Potentially high crystal quality and lower operating costs make the method very attractive for commercial applications, but in practice, industrial applications have remained limited to date (Fernandéz-Torres, et al., 2012).

The aim of this thesis is to study the commercial and technological feasibility of producing sulphate products from mining water concentrate using EFC. The case of study is the bioleach mine in Sotkamo, Finland, whose boreal conditions are ideal for cold separation. The objective is to identify promising sulphate products, test their production with laboratory-scale EFC experiments and evaluate the results for commercial potential. The ultimate goal is to find a product that does not overly complicate the mining process, is efficient to produce with EFC and has profitable market potential.

The thesis comprises of a literature review, applied experiments and result evaluation. The literature review describes the relevant mining processes, potential sulphate products and EFC technology. The aim is to understand how the process and potential products affect each other and how EFC can be applied effectively for intended production. The experimental part seeks to test a selection of individual sulphates for their eutectic crystallisation behaviour, and then apply EFC to synthetic and actual mine water concentrate. The results are evaluated to see if EFC could be applied to the mining process. Finally, an economical evaluation of a hypothetical EFC process is carried out to study its potential profitability.

2 Literature review

The aim of this part is to give a literature overview of the concepts and processes behind and leading up to sulphate extraction using EFC. The review gives a description of mining processes used to extract metals, water usage in mining, water recovery through reverse osmosis and possible sulphate products that could be gained from RO concentrate. Finally, EFC theory, application and mine water suitability are described.

2.1 Metal mining processes

Sulphate-rich water concentrates can be the product of a variety of metal mining processes. This chapter gives an overview of common mining methods, from ore extraction to extractive metallurgy.

2.1.1 Ore extraction

Initial ore extraction in mining can be divided into two approaches: surface mining and underground mining. Surface mining includes methods that create an open-air mining site that is often easily accessible by vehicles and personnel. Surface mining is very popular due to its high productivity, low operation costs and good safety. In the United States, for example, 98 % of metallic ores are surface mined (Hartman & Mutmansky, 2002). Surface mining is best suited to shallow deposits, which require minimal earth removal. A common surface approach is strip mining, where strips of overburden earth are removed to open an ore deposit (McLemore, 2008). An alternate method is open pit mining, where ore and waste (all non-ore earth) are extracted in an open-air pit. Open pit waste material is usually either stored or used in site construction, such as in roads and walls. If the mine is closed, the stored waste can be reintroduced into the pit. This is especially

important for environmental preservation, as open pit mining can cause significant strain on nature when large amounts of earth are removed (Riekkola-Vanhanen, 2013). Underground mining is used with deep deposits where tunnelling is more feasible than an open-air site. This type of mining requires more extensive auxiliary operations than surface mining due to higher safety risks. Structural supports, air ventilation, lighting and communications are some of the operations crucial in underground mines. (Hartman & Mutmansky, 2002)

The ore can be mined with a variety of suitable methods, such as pit drills, crushing fragmentation and blast fragmentation, depending on the deposit. The subsequent processes affect how the ore is handled: hydrometallurgical methods, for example, generally require fine agglomerated ore particles to increase solution contact area (Riekkola-Vanhanen, 2013). Therefore, the ore may be crushed and treated in several steps after initial extraction.

2.1.2 Extractive metallurgy

The choice of metallurgical methods used to process minerals defines much of the chemical needs and outputs of a mine, and therefore significantly affects wastewater generation. Extractive metallurgy consists of concentrating or directly refining metals from their mineral ores. Like ore extraction, metallurgical methods are suited to different types of deposits.

Pyrometallurgy consists of high-temperature processes that are based on extracting pure metal from ore by thermal breakdown and reduction reactions. In practice, minerals (often metal sulphides) are converted to oxides and then reduced to their pure forms (Kikuchi, et al., 2009). Due to their high-energy nature, pyrometallurgical methods have fast reaction and output rates. The speed is aided by the capability to make use of exothermic

energy of the minerals themselves, which works best with concentrated material. This makes pyrometallurgy best suited to high-grade ore that can offset energy requirements of the extraction. In addition, the processes can often use energy from hydrocarbon fuels directly, without depending on just electrical power (Hayes & Jak, 2014). Pyrometallurgy is usually divided into roasting and smelting to oxidise and refine the minerals, respectively. The refining uses a reduction agent, such as coke or another carbon source, to produce liquid elemental metal (Kikuchi, et al., 2009). Due to its high-energy nature, pyrometallurgy usually only uses water for auxiliary applications, such as washing and cooling, leading to lower amounts of wastewater compared to water-based processes.

Processes that depend heavily on water fall mainly under hydrometallurgy, a field that uses aqueous solutions to dissolve and transport metals from ore. The metals are dissolved, or leached, by an acidic or alkaline solution that transports the metals as intermediary compounds, such as sulphates. The process is often slow compared to pyrometallurgy, but able to utilise low-grade deposits much more efficiently. Hydrometallurgical process streams are therefore dilute in comparison (Hayes & Jak, 2014). Global metal demand is constantly increasing, but high-grade deposits suitable for traditional extraction are decreasing. The situation has motivated increased use of methods suitable for low-grade deposits, such as hydrometallurgy (Brierley, 2010). Hydrometallurgy is also capable of selectively leaching a wider variety of ores and minerals due to the many chemical reaction paths available (Watling, 2008).

In practise, leaching can be applied in several ways. The ore can be leached directly by introducing leaching solution through holes drilled into the ground and collecting the pregnant leach solution (PLS) with sumps, which is called *in situ* leaching. However, minimising loss of PLS into groundwater can be difficult (Hayes & Jak, 2014). An alternative is piling the ore into heaps that are irrigated with the leach solution and leached for months to maximise

effectiveness. After a leaching cycle or two, the ore heaps can be covered and re-vegetated to minimise environmental impact of the mine (Riekkola-Vanhanen, 2013). Leaching can also be done in reactors to reach higher speeds and efficiencies. The reactor vats can be stirred (agitation leaching) or leaching solution can simply be percolated through the ore (Hayes & Jak, 2014).

The subset of biohydrometallurgy uses bacterial biocatalysis to enhance its leaching reactions. This so-called bioleaching is based on choosing leaching conditions that are compatible with naturally occurring ore bacteria. The catalysis speeds up key oxidation steps, leading to more effective leaching (Halinen, 2015). The pH of a bioleach solution is kept at an optimal level for the bacteria involved, which are often acidophilic. Organism behaviour is also optimised by controlling leaching site temperature and ventilation (Riekkola-Vanhanen, 2013).

Hydrometallurgy requires a metal recovery step to extract metal compounds from the PLS stream. The separation can be done with, for example, chemicals or electrolysis. In chemical separation, metal compounds are precipitated from the process stream by adding suitable chemicals. The process is often carried out through several steps to precipitate metals selectively (Riekkola-Vanhanen, 2013). An example of precipitation steps is presented in Figure 1.

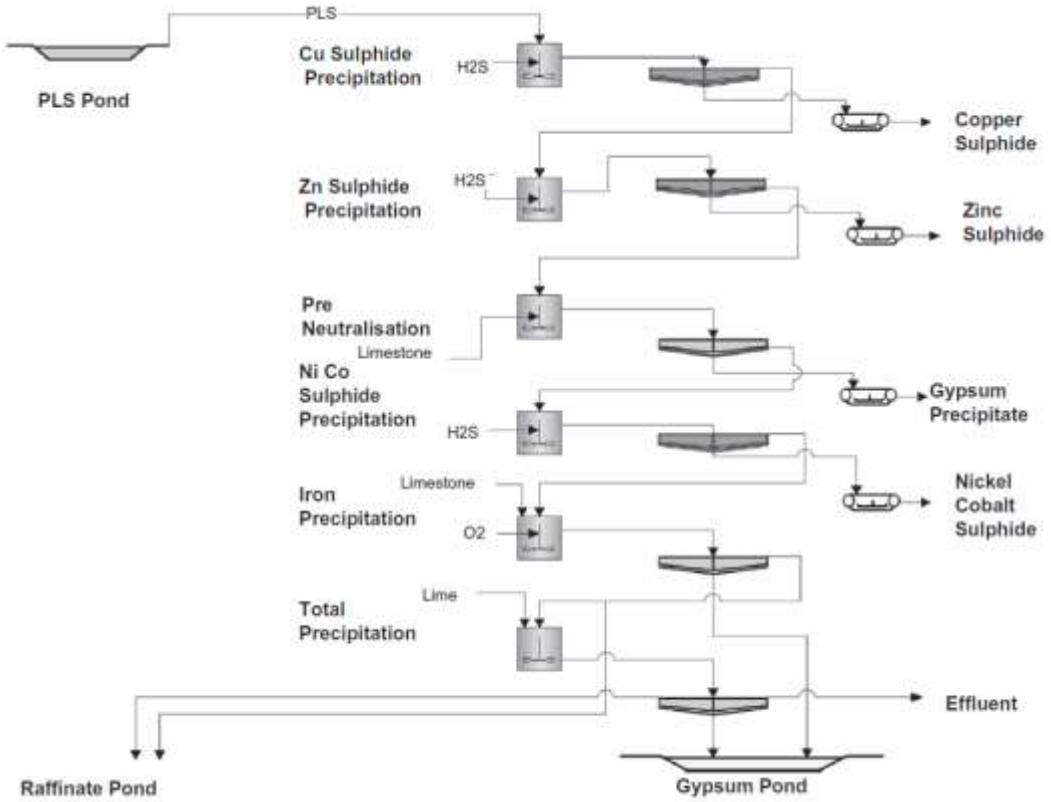

Figure 1. Chemical metal recovery steps in a bioleach mine. (Riekkola-Vanhanen, 2013)

Metal recovery can also be carried out through electrolysis, a field, which is sometimes called electrometallurgy. Electric current is used to drive redox reactions that reduce a metal to its pure form. Unlike sulphide precipitation, electrolysis metal recovery, or electrowinning, can therefore be used as the final refining step (Hayes & Jak, 2014). Since the metallurgical methods are suited to different materials and concentrations, a large mining process may use a combination of them in parallel or sequence (McLemore, 2008). Metal sulphides precipitated from a hydrometallurgical stream, for example, require additional refining, which may be done through smelting or roasting. This way, leaching can be used to concentrate metal content to make it more suitable for pyrometallurgy, or refined directly with electrowinning.

2.2 Mine water management

Many mining processes create significant amounts of effluent, which cannot be directly discharged if its salinity exceeds regulations. This chapter describes the sources of affected water in mines, why water treatment is necessary and how water can be recovered through reverse osmosis technology.

2.2.1 Mine water balance

Water is an important part of a mining process, and is used both directly in mining and in auxiliary operations. Direct heavy water use can begin in ore extraction. Hydraulicking, for example, is based on using high-pressure water erosion to displace ore (Hartman & Mutmansky, 2002). Hydrometallurgy is another water-heavy operation due to its reliance on aqueous streams for leaching and transportation. Auxiliary uses include dust suppression, cooling, washing and personnel usage (Kemp, et al., 2010). Much of the water is not physically consumed in these processes, but it accumulates contaminants and becomes affected water. The result for mine management is that processes that consume large amounts of water can also generate affected water in equal amounts.

Depending on the combination of processes, the water balance may be positive, where the process generates excess affected water, or negative, where the process consumes water. Positive water balance usually forces processes to remove effluent through a discharge stream. However, temporary changes in water amounts, such as heavy rainfall on an open process, may force a discharge even from a clearly water-negative site (Marsden & House, 2006).

2.2.2 Water treatment demand

Affected water is a major problem for mines due to its chemical composition, which prevents its disposal into mine surroundings without treatment because of possible environmental effects. The main problem components of affected water are acidity and salinity (composed mainly of metal and sulphate ions) (Maila, et al., 2014). Acid mine water has been a longstanding issue that is responsible for much of the demand for better mine water management (Kemp, et al., 2010). Spillages of acid mine water have been observed to cause significant pH changes in nearby waters, which can cause adverse effects for local ecosystems (Banks, et al., 1997). Acidity has the strongest impact on naturally acidic soil types that have little to no pH buffering ability, and reactions caused by increased acidity can release toxic substances like arsenic and cadmium (Pöyry Finland Oy, 2011).

Salinity is mainly composed of dissolved metals and sulphate. The presence of sulphate is often the result of processing metal sulphide minerals, common sources of mined metal (Hayes & Jak, 2014). Metal ions of more than trace concentration are generally products of chemicals added into the process, such as in metal recovery and neutralisation. Some common examples are NaOH and $Mg(OH)_2$, which contribute sodium and magnesium, respectively (Halinen, 2015). Increased salinity has been observed to have environmental effects, such as the ones described by van Dam et al. (2014) and Salmelin et al. (2016), but in practice affected water composition and volume must fall within government-regulated values (Pöyry Finland Oy, 2011). An example of ion composition of neutralised mine water is presented in Table 1.

Table 1. Chemical and compositional information of two nickel mine water samples. (van Dam, et al., 2014)

Analyte	Mine sample 1	Mine sample 2
pH	7,6	8,0
Conductivity (µS/cm)	2320	3090
Dissolved organic carbon (mg/l)	0,8	1,3
Ca (mg/l)	240	320
K (mg/l)	8,3	10
Mg (mg/l)	200	240
Na (mg/l)	84	96
Cl (mg/l)	21	24
HCO_3 (mg/l)	210	210
SO_4 (mg/l)	1300	1800

To solve their water problem, mines often raise the pH of the water to alkaline levels, usually using lime or limestone. The approach neutralises the acidity and causes many accumulated substances to precipitate as ion compounds, such as hydroxides and sulphates in so-called neutralising ponds (Johnson & Hallberg, 2005). Depending on the process, water overflow from the ponds can be pure enough for discharge, but in certain water compositions, additional treatment is required. Reducing affected water ion levels by modifying the mine process chemistry itself is would be a difficult and costly undertaking, so water recovery through methods such as reverse osmosis is a more feasible option.

2.2.3 Reverse osmosis water recovery

A solution to high effluent volumes is water recovery through reverse osmosis (RO). RO is a membrane technology that is used to desalinate water, leaving high-purity water and concentrated saline solution as products. In natural osmosis, water migrates naturally by diffusion from a lower concentration solution to a higher concentration through a semi-permeable membrane (letting only water pass), equalising the concentrations in a closed system. Osmosis creates pressure towards areas of higher concentration,

called osmotic pressure. In reverse osmosis, forced pressure (higher than natural osmotic pressure) is used to drive water into the low concentration area instead. Like in natural osmosis, the water pushes through a membrane that passes water in preference to solutes. The membrane is an effective purifier because permeants can dissolve into the membrane itself and diffuse through it to the other side. (Wenten & Khoiruddin, 2016)

RO separates substances based on molecular size and charge. As a molecule of relatively low mass and neutral charge, water easily passes through the membrane. Since most contaminant salts have much higher molecular masses and are dissolved as their component ions (Na_2SO_4 dissolved as Na^+ and SO_4^{2-}, for example), they are unlikely to pass, especially in low concentrations (Lee, et al., 2016). This makes RO particularly effective for purifying saline solutions encountered in mining, especially as up to 99% of salts can be removed in practice (Wenten & Khoiruddin, 2016).

The membrane itself is the most significant component of an RO process. The crucial properties of an RO membrane are chemical and mechanical durability, water permeability and salt rejection. Chemical durability is required to tolerate a multitude of substances without taking immediate and long-term damage, with higher durability materials being chemically versatile. Mechanical durability is necessary when the pressure and flow of the system are high, so the membrane can function without tearing from the stress. Water permeability is an especially critical factor, since higher permeability decreases the energy required to overcome osmotic pressure and makes the process more efficient. However, high water permeability generally comes at the cost of salt rejection rate, so maximising both parameters can be challenging. The two most used membrane materials are cellulose acetate and polyamide. The latter has become more widely used as its composite nature gives it versatile properties. (Lee, et al., 2016)

Membrane fouling is a significant vulnerability in RO. Whether of biological or chemical origins, any solid build-up on the membrane surface will hinder water permeability and may decrease salt rejection as well. In mine affected water treatment, inorganic fouling is generally dominant (Wenten & Khoiruddin, 2016). When the retentate solution reaches high concentrations, dissolved salts may start precipitating on the membrane. As maximum water recovery is often the goal, inorganic scaling is a very common problem. Several different approaches are used to mitigate or prevent membrane fouling, including feed pre-treatment, membrane modification and use of anti-scaling chemicals. Pre-treatment consists of methods to minimise and prevent precipitation, such as pH changes or removal of interfering substances and solids by filtration. Modifying the membrane itself is a potentially effective long-term solution, in which a membrane is fine-tuned to withstand specific conditions. However, sufficient modification may be difficult, as a complex feed solution may have several substances to take into account. In addition, fouling-resistant membranes may decrease permeability. Anti-scaling agents are chemicals that aim to prevent substances from precipitating on the membrane surface by increasing their solubility and interfering with crystal growth, and are more readily used than specialised membranes due to ease of use and lower cost. (Puretec Industrial Water, 2017)

Reverse osmosis has proven to be effective in treating mine water streams. Even with complex mine waters, RO has been found to retain high water recovery rates (Randall, et al., 2011). Kyllönen et al. (2016) observed water recovery up 60 % in their study. However, large volumes will still leave significant amounts of saline brine. Treating the brine further has two advantages: approaching complete water recovery and producing solid salts that may be viable commercial products, improving treatment economy.

2.3 Concentrate sulphate products

Crystallising dissolved ions is a way to pursue very high water recovery. The salts also present a commercial opportunity as chemical products if extracted with high purity. A possible group of product compounds are sulphates. This chapter aims to identify potential sulphate compounds and describe their properties, market potentials and possible crystallisation options.

2.3.1 Potential sulphate products

Any possible products gained from RO concentrate are defined by the brine composition. Sulphide ores are a major source of mined metals (Hayes & Jak, 2014), and sulphide extraction is a common source for sulphate presence in mine water, especially in bioleaching due to its aqueous reactions (Vera, et al., 2013). Mine waters also contain various cations that form ion compounds with sulphate, so sulphate salts present a clear opportunity for solid products that could improve the economy of RO concentrate treatment (Randall, et al., 2011). However, the properties of possible sulphates can differ significantly, so their feasibility must be considered individually. An example of RO mine water concentrate's composition is presented in Table 2.

Table 2. Ion concentrations in South African mine water RO concentrate. (Randall, et al., 2011)

Ion	Concentration (mg/l)
Na^+	6720
K^+	1810
Ca_2^+	1340
Mg^{2+}	75
NH_4^+	42
SO_4^{2-}	16000
Cl^-	955
NO_3^-	398
HCO_3^-	61

Considering the brine composition in Table 2, sodium is clearly the cation with the highest concentration. Therefore, sodium sulphate would be the primary product in this case. However, as the individual chemistry and source ore of a process determines brine composition, the relative cation concentrations can vary between mines. For example, the mine water sampled by van Dam et al. (2014), seen in Table 1, had calcium and magnesium as the cations with highest concentration. Maila et al. (2014) studied the use ammonium hydroxide for mine water neutralisation, which would generate effluent with relatively high ammonium levels. Therefore, it is useful to consider the sulphate salts of several cations that could have the highest concentration in affected water.

Sodium sulphate (Na_2SO_4) is one of the common possible brine products, and can be the product of chemicals such as sodium hydroxide. The salt's stable forms are presented as a phase diagram with water in Figure 2.

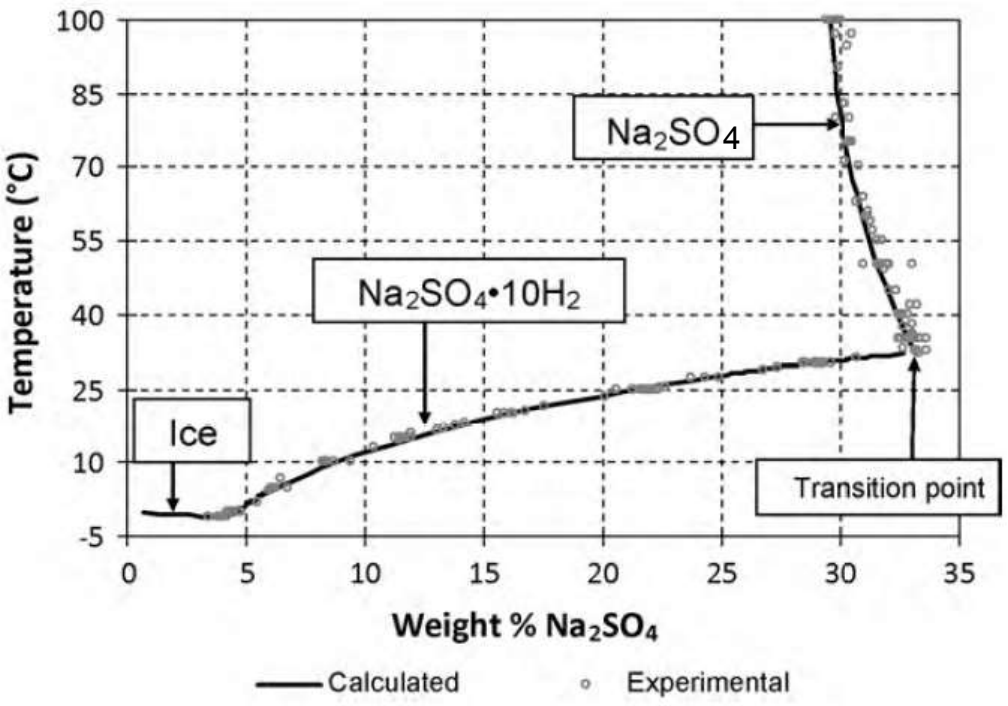

Figure 2. Binary phase diagram for water-Na_2SO_4 system. (Lewis, et al., 2010)

The phase diagram shows that the decahydrate form is dominant in areas of moderate to low temperature and concentration, which are typical for mine water (Reddy, et al., 2010). Therefore, $Na_2SO_4 \cdot 10H_2O$ is the likely form as an effluent product. A Chemical Economics Handbook report (IHS Markit, 2016) notes that sodium sulphate is mainly used in detergents, a use that is decreasing in US and Europe but stable or increasing in developing nations. It is also stated that sources for the salt are mostly either natural minerals or industrial processes, where sodium sulphate is a side product. A collection of trader prices on Alibaba.com and Guidechem.com gives anhydrous sodium sulphate an average of 77,1 €/ton (see Appendix I for source breakdown).

Potassium sulphate (K_2SO_4) is a possible major product for processes with significant potassium addition, such as from potassium hydroxide. Unlike sodium salt, potassium sulphate does not have hydrate crystalline forms. K_2SO_4 is rarely found in pure form, and must instead be processed from mixed minerals or produced chemically. The salt is mainly used as a fertiliser, as potassium is an important element for plant growth. Compared to rival fertiliser potassium chloride, the sulphate also brings in beneficial sulphur without adding chlorine, which is harmful to some crops. (International Plant Nutrition Institute, 2017)

Root vegetables and coconuts are examples of crops that react unfavourably to chloride (Swamy & Majumdar, 2013). Frost & Sullivan market research (2014) and a collection of trader prices on Alibaba.com and Guidechem.com gives potassium sulphate an average of 485,5 €/ton (see Appendix I for source breakdown).

Magnesium sulphate ($MgSO_4$) is another major possibility, usually as a product of magnesium hydroxide or the ore itself (Halinen, 2015). It has anhydrous and hydrate forms, with the heptahydrate, or Epsom salt, being common. A salt-water phase diagram showing different hydrate regions is presented in Figure 3. The magnesium and sulphur content give the salt uses

in agriculture and food as a nutrient (Rao & Kawamura, 2007). Magnesium sulphate also has many applications in medicine due to its beneficial effect in treating several conditions (Hunter & Gibbins, 2011). A collection of trader prices on Alibaba.com and Guidechem.com gives magnesium sulphate an average of 103,7 €/ton (see Appendix I for source breakdown).

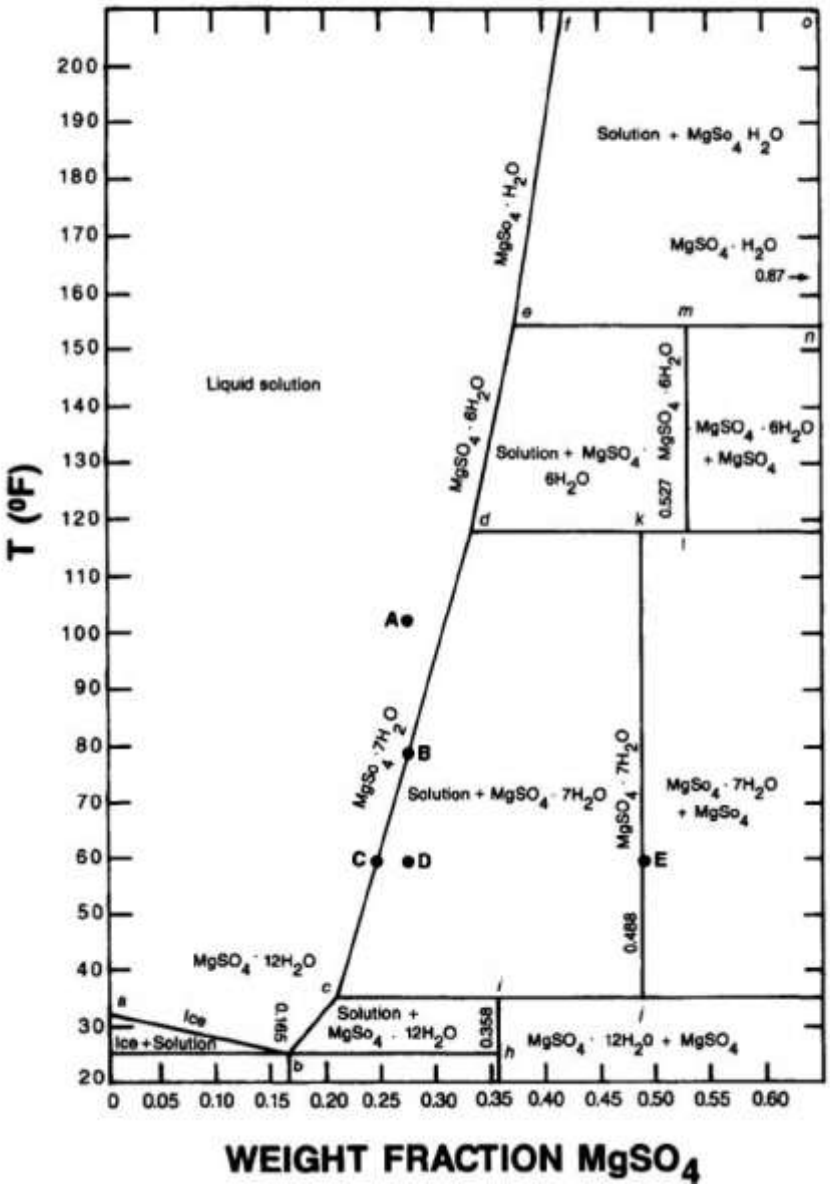

Figure 3. MgSO4-water phase diagram. (Myerson, 2002)

Ammonium sulphate ($(NH_4)_2SO_4$) can be the product of chemicals such as ammonia. Ammonium sulphate is highly soluble in water and forms no

hydrates. The salt's nitrogen and sulphur content make it useful as a fertiliser, though the low nitrogen content in the compound limit its competitiveness (International Plant Nutrition Institute, 2017). A collection of trader prices on Alibaba.com and Guidechem.com gives ammonium sulphate an average of 128,3 €/ton (see Appendix I for source breakdown).

A summary of average trader prices for sulphates is presented in Table 3.

Table 3. Summary of average sulphate prices from quoted sources (see Appendix I).

Chemical	Na_2SO_4	K_2SO_4	$MgSO_4$	$(NH_4)_2SO_4$
Avg. Price (€/ton)	77,1	485,5	103,7	128,3

As can be seen from the average prices, the sulphates significantly vary in market value. Potassium sulphate appears especially commercially attractive. The future market potential of K_2SO_4 also appears stable or growing. In a Frost & Sullivan market report for Western Europe (2014), potassium sulphate's share in potassium fertiliser use was expected to rise due to its use for chloride-sensitive crops. Furthermore, potassium fertilisers were estimated to have the highest growth rate of all nutrients up to 2020.

In Asian and Pacific countries, potassium chloride was mostly dominant due to increasing awareness about sulphate toxicity (Swamy & Majumdar, 2013). However, crops vulnerable to chloride have left a small market portion for the sulphate. The area was predicted to see increasing potassium fertiliser demand, which was expected to increase prices due to decreasing reserves. In comparison, the Western Europe sulphate share was expected to rise (Rajagopal & Majumdar, 2014). Agreeing with Frost & Sullivan's analysis, recent market study by BBC Research (2017) predicted potassium to be the fertiliser group with the highest international growth rate up to 2021, with potassium sulphate having the second highest growth.

2.3.2 Sulphate crystallisation methods

Extracting sulphate salts from RO concentrate brine is a process that can be carried out through several methods. As ionic compounds, the sulphates take crystalline solid forms, which can be produced with a variety of crystallisation methods (Myerson, 2002). Crystallisation occurs when a solute's concentration is above its solubility in the solvent (water). Induced crystallisation is based on creating this imbalance by changing the system through one or more ways, including removing solvent, changing temperature or pressure, and adding additional substances (as solutes or solvents) (Mullin, 2001). From a commercial perspective, the optimal crystallisation method would produce high-purity crystals at a fast rate without high operation and investment costs. In practise, a compromise of these parameters may be necessary.

A well-known and common method is evaporative crystallisation (EC), where solvent is evaporated to increase solute concentration. The technique's oldest and easiest application is an open-air pool that uses solar evaporation to crystallise dissolved ions, most commonly to produce salt. In industrial use, EC is also used in continuous processes, where the entire solvent volume is not necessarily evaporated. Complete evaporation is also impractical if the solution contains unwanted elements, which will contaminate the product crystals. Despite its technical simplicity, evaporation requires large amounts of energy, which leads to significant cost when open-air systems are not feasible. Industrial evaporation processes are generally defined by high energy costs. (Fernandéz-Torres, et al., 2012)

Reactive precipitation is another way to separate dissolved salts. The technique involves mixing the solution with a reagent, usually causing very fast crystallisation. The reaction may be quite complex to be analysed, and therefore crystal quality may vary greatly. In addition, complex solutions may be difficult to match with suitable reagents (Mullin, 2001). From a

commercial perspective, the method brings additional chemical costs and supply demands. When dealing with mine water concentrate, the problem of adding more chemicals into the water to be purified becomes an issue of its own. Fast precipitation may also leave the product crystals vulnerable for contamination during nucleation. Precipitation can also be achieved by adding non-reactive substances, such as another salt that reduces solubility ("salting out"). This has the advantage of negligible energy costs and higher crystal purity, but it requires additional chemicals (Mullin, 2001).

When solubility decreases with temperature, crystallisation can also be induced by cooling the solution to supersaturation. Cooling crystallisation is particularly effective for high concentrations of low-solubility salts, as most of the dissolved salt can be crystallised above 0 °C. However, it is also limited by solubility, which means not all salt content can be crystallised (van der Ham, et al., 1998). Therefore, near-complete purification is unfeasible. Cooling requires heat transfer but energy costs can be much lower than with evaporation, as heat of fusion is relatively low (Mullin, 2001).

All of the described crystallisation methods have advantages and disadvantages, with important parameters being product quality, level of water purification and costs. However, this study aims to explore an additional option: eutectic freeze crystallisation. The method has the potential to maintain high product quality, effective water purification and low operation costs. Therefore, it is an attractive approach to creating a viable sulphate side product from mining water concentrate and is described in more detail in chapter 2.4.

2.4 Eutectic freeze crystallisation

Crystallising salts from a solution at their eutectic points is a separation method that is based on long-known principles, but has not yet found wide application in industry. EFC has the potential to be a low-cost yet effective technique that is capable of producing high-quality solid products. This chapter describes the theoretical background of EFC, its practical application, considerations in process and equipment design and the suitability of EFC in producing the selected sulphate options from mine water concentrate.

2.4.1 Theoretical basis

Eutectic freeze crystallisation is based on separating a dissolved salt from an aqueous solution by cooling it to its eutectic point. At the eutectic point, ice, salt and the solution exist in an equilibrium that is defined by both temperature and concentration. Therefore, at eutectic point it is possible to simultaneously crystallise both ice and salt without solidifying the entire solution. A phase diagram illustrating the dynamics is presented in Figure 4Figure 4.

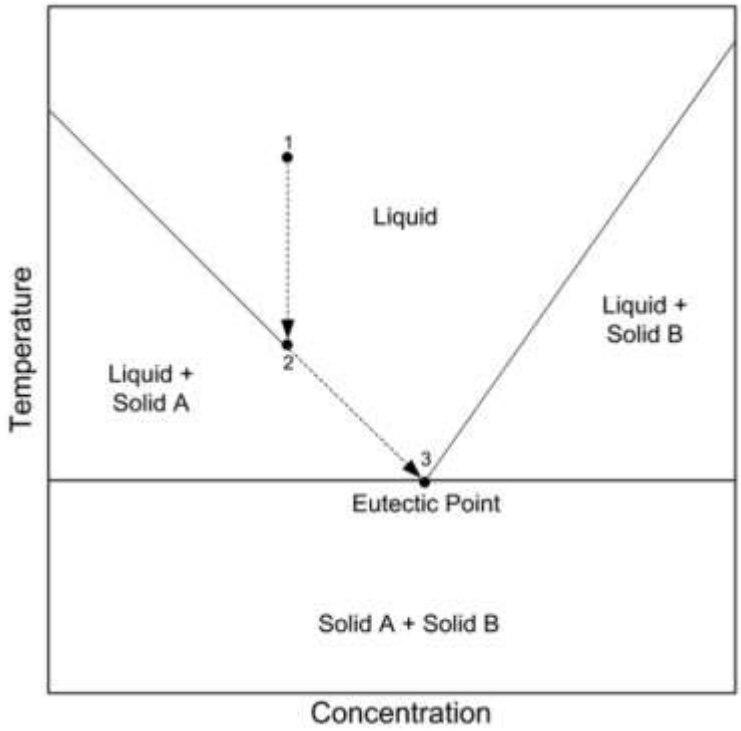

Figure 4. Eutectic point shown in a binary phase diagram. (Randall, et al., 2011)

Points 1 through 3 in Figure 4 represent cooling a solution at a concentration below the eutectic point. In that area, ice will crystallise first (point 2), causing the concentration to increase and the crystallisation temperature to drop, requiring further cooling. At the eutectic point (point 3), equilibrium is reached and salt crystallises. Conversely, in original concentrations higher than the eutectic point, salt will crystallise first and the concentration decreases. Cooling a solution at the precise eutectic concentration will result in simultaneous crystallisation of ice and salt. However, a solution is unlikely to be at eutectic concentration, so longer crystallisation paths are more common. (Randall, et al., 2011)

The eutectic point is unique to each solution, and its temperature and concentration points may change significantly between compositions. In practice, the difference is seen in salt solubility and crystallisation points of all components. Small additions of impurities (ions previously not present in the solution), for example, have been observed to slightly lower the eutectic temperature. Randall et al. (2011) noted the effect in their experiments. In

significant amounts, multiple salts can form a single eutectic point where two or more salts crystallise. The new eutectic point can be significantly different if the salts' properties are not similar. One such case was observed by Reddy et al. (2010) with Na_2SO_4 and NaCl. In addition to eutectic temperature drop, added sodium caused Na_2SO_4 to individually crystallise earlier due to decreased solubility. The event was explained by the common ion effect, caused by the salts sharing the cation. Differences in eutectic temperatures for Na_2SO_4-systems are presented in Table 4.

Table 4. Eutectic temperatures of different systems with Na_2SO_4.

System	Eutectic temperature, °C
Na_2SO_4-H_2O	-1,24
Na_2SO_4-H_2O with minor impurities	-2,22
NaCl-Na_2SO_4-H_2O	-21,22

Due to large differences in eutectic temperatures, information on the phase behaviour of the solution must be detailed in order to accurately predict the crystallisation process. In complex hypersaline brines, this may be very difficult, as literature data on multi-salt solubility is often limited. The result is that appropriate phase diagrams may not be available, and in the case of systems with more than four ions, phase diagrams become impractical compared to more complex simulation (Lewis, et al., 2010). Complex brines may have different areas of crystallisation that depend on solution temperature. Therefore, it is theoretically possible to crystallise individual salts through specific eutectic temperatures (Randall, et al., 2011). This becomes difficult when two or more salts share crystallisation temperatures (Randall, et al., 2009). An example of a multi-salt system's areas of crystallisation is presented in Figure 5.

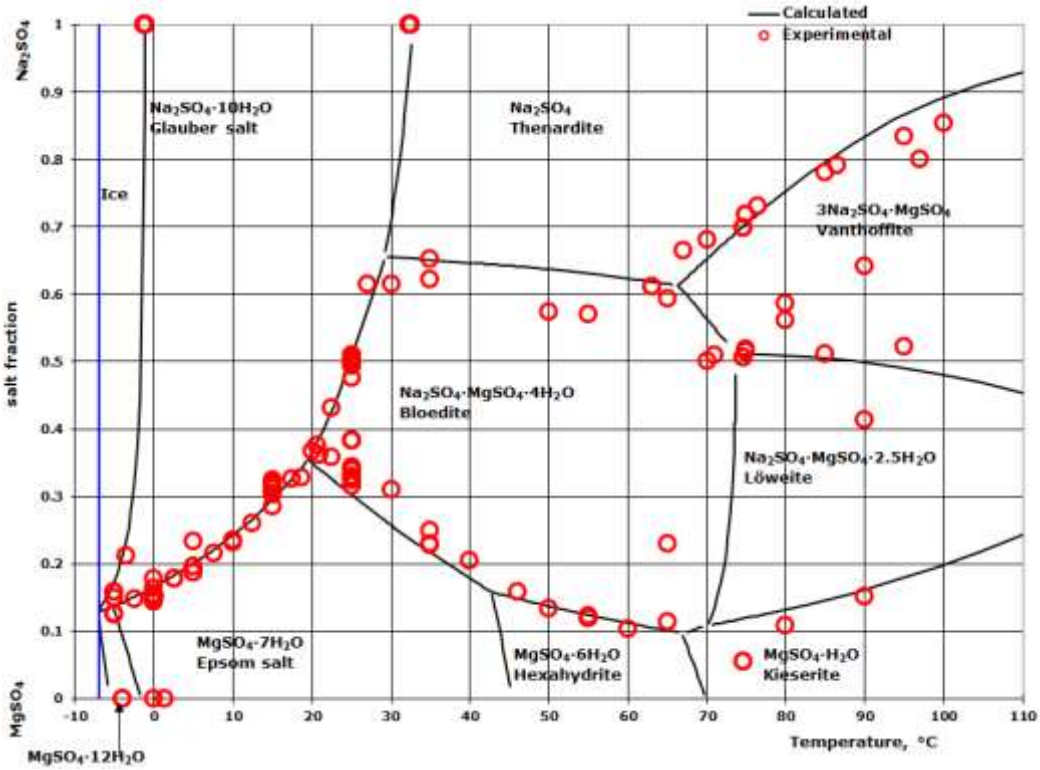

Figure 5. Phase diagram of the Na_2SO_4-$MgSO_4$-water system, showing crystallization areas. (Aqueous Solutions Aps, 2017)

When a solution is initially cooled, the path to its eutectic point is governed by crystallisation mechanics. Crystallisation does not occur immediately when the solution passes a solubility or freezing line. Instead, the solution becomes supersaturated (Myerson, 2002). Supersaturation is the thermodynamic driving force behind crystallisation and higher supersaturation leads to increased crystallisation. However, crystals cannot form without centres of crystallisation. Nucleation processes determine the forming of these centres and subsequent crystal growth (Mullin, 2001).

Nucleation can happen through primary, secondary or combined processes. Secondary nucleation involves the growth of new nuclei on an existing parent material, such as solid salt or ice crystals. Secondary nucleation requires the least amount of supersaturation to occur spontaneously, so it is the most likely process to happen in the presence of a seed material (Randall, et al., 2009). If no parent material is present, crystallisation centres are created through primary nucleation. The nuclei are either formed on a solid surface

due to impurities (heterogeneous nucleation) or in the bulk solution itself (homogenous nucleation). Due to lack of existing nuclei, unlike in secondary nucleation, primary nucleation requires more supersaturation to take place spontaneously (Mullin, 2001). Areas of primary and secondary nucleation also overlap, creating an area where unseeded nucleation is unpredictable. The areas of nucleation are presented in Figure 6.

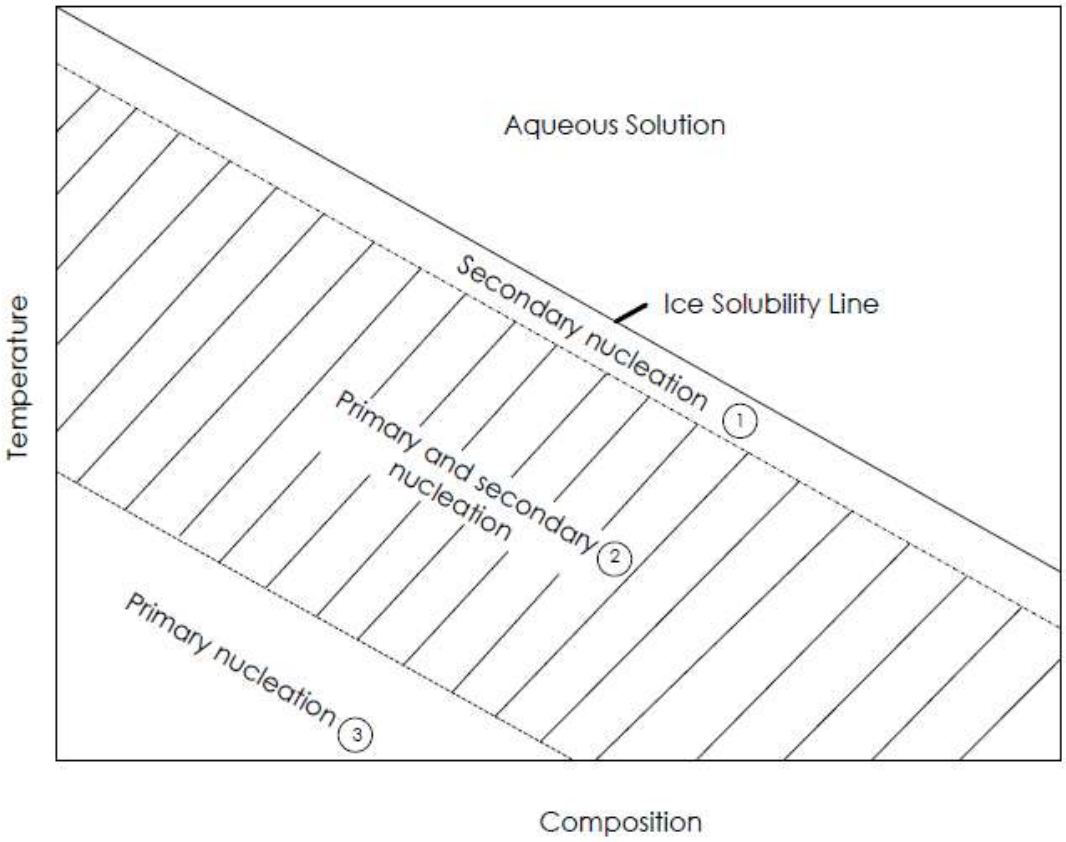

Figure 6. Nucleation regions in an aqueous solution. (Randall, et al., 2009)

Region 2 in Figure 6 is where both primary and secondary nucleation can occur. The exact point where nucleation takes place varies: the first nuclei are formed by random interactions of solute particles, which in turn promotes additional nucleation (Randall, et al., 2009). This stochastic nature of unseeded nucleation means that the initial crystallisation temperature is unpredictable in the same system. Increased cooling and therefore supersaturation increases the probability of nucleation due to higher thermodynamical driving force. The exact mechanisms of homogenous

nucleus formation are largely unknown, adding to the unpredictability (Mullin, 2001).

Initial nucleation can be made more repeatable by using seed crystals. As mentioned earlier, present parent material will make secondary nucleation very likely, so adding seed material after crossing the solubility line will promote higher temperature nucleation. Ice and salt can be seeded separately in order to promote the formation of either. If seeding is done in the region of combined primary and secondary nucleation, crystallisation is often immediate. However, cooling the solution beyond secondary nucleation region also risks spontaneous nucleation, the probability of which increases with supercooling. In complex systems of interfering salts, selective seeding can promote one salt over another, aiding difficult separation. (Randall, et al., 2009)

One of the reasons EFC is an attractive option is that the energy consumed by water in crystallisation, the heat of fusion, is relatively low. The heat of water evaporation, for example, is over six times higher (Randall, et al., 2011). This gives EFC a significant theoretical advantage over evaporative crystallisation in energy requirements, and therefore operation costs. The advantage could be even greater in boreal conditions, where low ambient temperatures might function as a pre-cooling step for EFC but hinder evaporation. Selective crystallisation is another useful EFC feature. Even in complex systems, EFC can be used to crystallise a single salt product, and impurities simply cause variance in the eutectic point, such as in the experiments by Reddy et al. (2010). This crystallisation behaviour also means that the solid salt is very pure, since impurities in the crystals are usually only found in trace amounts. Evaporation tends to create mixed salts, often resulting in impure products. Ammonia, for example, easily contaminates EC-produced salts but does not affect EFC beyond any other non-crystallising impurity (Lewis, et al., 2010).

As a separation method, EFC has the feature of complete solution conversion to ice and salt. The result is that salt yield is not limited by remaining solubility, which is an advantage over cooling crystallisation (van der Ham, et al., 1998). The relatively large difference in densities of ice and inorganic salts also enables natural separation by gravity, as ice floats to the solution surface and vice versa. Due to constant generation of ice and solid salt, EFC forms a natural steady state and can therefore be designed as a continuous process with relative ease (van der Ham, 1999).

2.4.2 Basic applied process

The core part of an applied EFC process is the crystalliser that is kept at eutectic temperature to produce ice and salt. When eutectic, the system's yield is controlled by the amount of heat transfer, or cooling (van der Ham, 1999). Using gravity separation, the product streams can be kept separate, so that ice and salt do not need a combined separation step. Layout of a basic binary EFC process is presented in Figure 7.

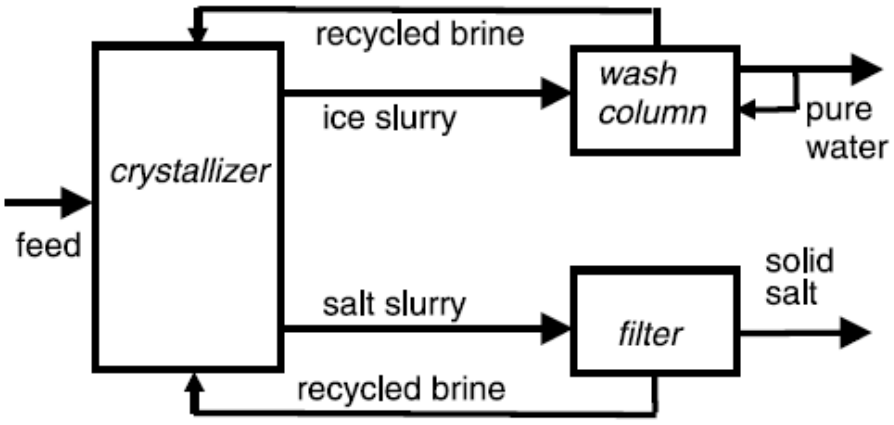

Figure 7. Basic EFC binary system. (van der Ham, et al., 2004)

Cooling the crystalliser is crucial for EFC operation, and a key part of it is the choice of cooling method. Cooling approaches can be divided into two categories: direct and indirect cooling. Direct cooling is based on adding a liquid cooling element into the solution itself. The coolant is a volatile refrigerant that transfers heat from the solution by evaporating, and therefore lowering solution temperature (van der Ham, et al., 1998). However, not all coolant evaporates, so the solution remains contaminated through all remaining parts of the process. Another effect is that the process must be pressurised in order to control the rate of evaporation. Indirect cooling, on the other hand, relies on heat exchanging surfaces to cool the solution. As the coolant is not in contact with the solution, the aforementioned complications of direct cooling do not apply. This has made indirect cooling a more popular choice, as the natural density separation of EFC can be harnessed more easily without the presence of a direct coolant. In addition, indirect cooling generally produces larger crystals, which are easier to separate (van der Ham, 1999).

Indirectly cooled EFC has certain details that need to be considered in apparatus design. The interface of fluid and the often-metallic heat exchange wall is vulnerable to crystal scaling, growth that can eventually cover the heat transfer area if left unchecked. Ice and many solid salts are good insulators, so scaling can significantly hinder heat transfer (Pronk, et al., 2008). Heat transfer interface is a likely platform for crystal growth because it has the lowest temperature in the system and, especially for a metallic surface, has the lowest energy barrier for nucleation (van der Ham, et al., 2004).

Several factors contribute to crystal scaling. Temperature difference between heat exchange wall and solution has been identified as one of these (Hasan, et al., 2017). Higher temperature difference increases crystallisation at the wall-fluid interface. As with the eutectic point, solution composition also has an effect on crystal scaling. Increased presence of non-crystallising component ions has been observed to slow down wall scaling. The effect was explained

by the components accumulating at the ice interface, obstructing further nucleation (Pronk, et al., 2008). When salt crystallises, the ice growth accelerates, as ions are removed from the interface. Pronk et al. (2008) also noted that scaling becomes observable when crystal growth on heat transfer walls increases beyond the rate of crystal removal, which is carried out by solution mixing and possible anti-scaling mechanics. In their study on ice growth on the cooling surface, Hasan et al. (2017) identified induction time, the time required for the initial scaling deposition process to begin, to be a key parameter in scaling control. Induction time was observed to be dependent on solution agitation, solution-coolant temperature difference, undercooling and residence time. Manipulating operation conditions for maximum induction time was said to extend scaling-free crystallisation.

Cooling issues lead to compromises in heat transfer. Higher temperature difference and heat transfer create greater product yields because of accelerated crystal growth, but worse crystal scaling is also a result. In addition to scaling issues, high heat transfer promotes fast nucleation, which creates crystals of smaller size. Large, slowly grown crystals tend to incorporate less or no impurities into their structure and are easier to wash (van der Ham, et al., 2004). Temperature difference can be lowered with minimal heat transfer loss by increasing transfer surface area, but in practise, a compromise is necessary due to the physical constraints of the crystalliser (van der Ham, 1999). Therefore, the maximum product output of a continuous eutectic freeze crystalliser may not be determined by the amount of cooling power available, but instead by the limitations of crystallisation behaviour.

2.4.3 Apparatus designs and industrial application

The aforementioned possible complications of an EFC process can make apparatus design difficult. However, functional continuous crystallisers have been successfully tested. One proven indirect cooling design for EFC is the cooling disk column crystalliser (CDCC). The apparatus is composed of a column that is cooled by several coaxially mounted disks. The feed stream enters the column through the middle and spreads inside the column through holes in the cooling disks. Upon crystallisation, ice floats up and salt gravitates down through the same holes, allowing for simultaneous crystallisation and separation. The top and bottom have their own outputs, producing an ice and salt stream, respectively. The cooling disks are equipped with scrapers to prevent ice scaling and to mix the solution. The basic CDCC layout is presented in Figure 8. (van der Ham, et al., 1998)

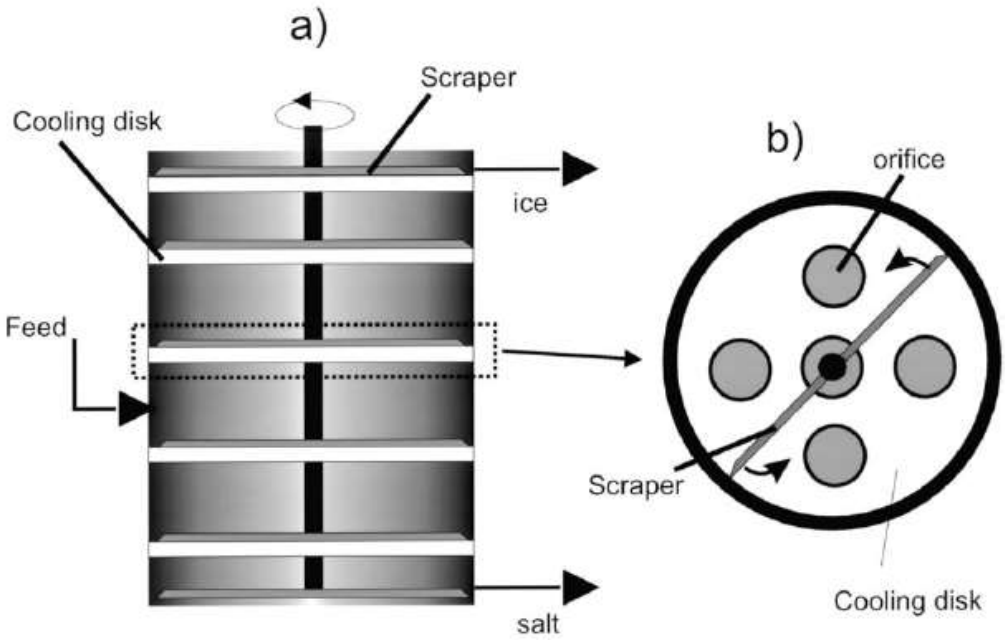

Figure 8. Cooled disk column crystalliser layout, with a) side view and b) top view. (van der Ham, et al., 1998)

Alternative anti-scaling designs have also been devised. Active crystal scraping results in limits and expenses on crystalliser design, so some research has been focused on non-mechanical options that might offer lower costs and more easily scaled-up processes. One of these is the fluidised bed heat exchanger (FBHE), which hinders scaling with fluidised particles that are introduced into the crystallising stream. The stream of inert particles is intended to prevent crystallisation on the heat exchange walls. The heat exchanger part itself is composed of vertical tubing within the solution tank. A fluidised bed heat exchanger schematic is presented in Figure 9. (Pronk, et al., 2008)

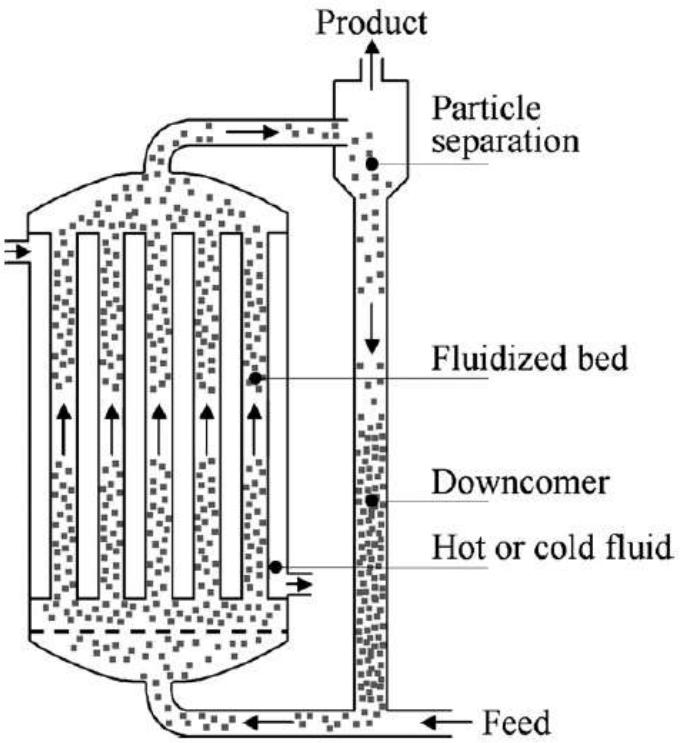

Figure 9. Fluidised bed heat exchanger. (Pronk, et al., 2008)

Fluidised beds have no active mechanisms inside the heat exchanger, so the design can be more efficient. Compared to CDCC-type equipment, fluidised bed exchangers usually have high heat transfer coefficients, and their investment cost per transfer area is lower. Additionally, the lack of active scraping is likely to lower maintenance needs. Therefore, the design is particularly attractive for large-scale industrial applications. An obvious

downside is that the gravitational separation of ice and salt cannot be achieved inside the crystalliser, as the fluidised particles must be separated first. However, the extra separation is relatively easy to implement and is not considered significantly detrimental to overall efficiency. FBHE has proven to be a promising crystalliser design, but it has been noted that the fluidised particles can be overcome by scaling, especially at eutectic point when salt ions no longer hinder ice forming. (Pronk, et al., 2008)

EFC's theoretical energy efficiency has been observed in applied processes. Compared to three-stage evaporative crystallisation, van der Ham et al. (1998) found EFC to have energy reductions up to 70%. A later life-cycle evaluation by Fernandéz-Torres et al. (2012) estimated EFC to use 6 to 7 times less non-renewable energy than EC, noting a lesser environmental impact in addition to efficiency. EFC can also be designed as a multi-stage process, but as observed by van der Ham et al. (1998), additional stages do not always add enough performance to offset increased cooling requirements. Dilute streams were noted to perform better with multi-stage EFC, due to the larger amount of water available for heat recovery.

Despite its promising features, large-scale industrial application of EFC has remained limited to pilot-level testing plants, such as in South Africa (Randall, et al., 2011). High initial investment cost has been identified as the primary obstacle, mostly caused by anti-scaling mechanics like scrapers (Hasan, et al., 2017). In his in-depth study of the economy of an EFC process, Vaessen (2003) found EFC capital investment costs to be higher than for an equivalent evaporative process. In a later study, Nathoo et al. (2009) found EFC investment costs to be up to 91% higher than for EC. However, it was noted that the numbers for EC were based on well-established technology, while EFC lacks the incremental improvements commonly seen in all industrial processes to date. Therefore, the difference in initial costs was expected to decrease as the method develops. Both studies found EFC to have lower operating costs, as was previously established.

2.4.4 Suitability for sulphate production

EFC's features seem to answer the needs of mine water concentrate treatment from several perspectives. The ability to extract a single ion product as a high-purity solid from a complex aqueous system is very attractive for sulphate production. The theoretical suitability has also been observed in practice. Studies such as by Randall et al. (2011) and Reddy et. al. (2010) successfully produced sulphate products out of complex affected waters. Metal sulphates in general have proven to be good crystallisation targets, even over a decade earlier by van der Ham et al. (1998). However, the complexity of mine waters means that different processes may need specific optimisation due to variation in crystallisation behaviour. As previously seen in Figure 6, differences in composition can cause significant changes to eutectic points. As noted by Reddy et al. (2010), the temperature range is feasible for crystallisation, but predicting exact eutectic conditions for mine water may be difficult.

Sodium sulphate has been a common EFC test subject, and has seen consistent success in production. Even from a multi-ion system, mirabilite ($Na_2SO_4*10H_2O$) crystals have been produced with EFC without detectable impurities (Reddy, et al., 2010). A key useful property of sodium sulphate is its relatively high eutectic temperature with water, which translates into lower cooling costs and complications. Eutectic temperatures between -1,24 °C (water system) and -2,22 °C (mining concentrate) have been often observed (Lewis, et al., 2010). Mining water concentrate tests such as the one by Randall et al. (2011) indicate that there are no significant obstacles to mining applications of sodium sulphate production by EFC.

Potassium sulphate has seen much less EFC applications than sodium sulphate. However, van der Ham et al. (2004) mentioned that the salt has

seen successful experiments with EFC and that there is no technological barrier to its production. Potassium sulphate has similar solubility to sodium sulphate at low temperatures (Seidell, 1940), which would indicate similar eutectic behaviour and possibly easy extraction. However, since potassium sulphate does not form hydrates, some crystallisation differences are possible.

Magnesium sulphate has notable differences to the last two candidates. The salt's solubility is several times higher than that of sodium sulphate (Seidell, 1940), which leads to different eutectic behaviour. As shown in Figure 3, $MgSO_4$ has its eutectic point with water around -3,9 °C and 17 wt.-%. One of the results is that the path to stable eutectic conditions may be more difficult, as large initial salt concentration or significant ice production is required. However, magnesium sulphate has been tested and found to be technically feasible to produce with EFC. Himawan et al. (2006) successfully crystallised magnesium sulphate dodecahydrate, though other hydrates such as heptahydrate were also said to be theoretically possible products.

Ammonium sulphate is a significantly different case to the previous ones. Due to its higher solubility (Seidell, 1940), its aqueous binary eutectic point is much lower compared to other presented sulphates. Phase data indicates the eutectic point to be around -19,35 °C and 40 wt.% (Xu, et al., 1998). The relatively low eutectic temperature would require more cooling power than the other salts, and reaching the eutectic point would be the most difficult of all sulphate options.

3 Case process description

The experimental part of this thesis explores the possibility of using EFC to produce sulphates from the concentrate of a mine in Sotkamo. The mine extracts metals such as nickel and zinc using a bioleaching process. The process uses open pit mining to collect and agglomerate ore that is leached in primary and secondary heaps. The dissolved metals are precipitated as sulphides, which are the final product form at the site. An overview of the mining process is presented in Figure 10.

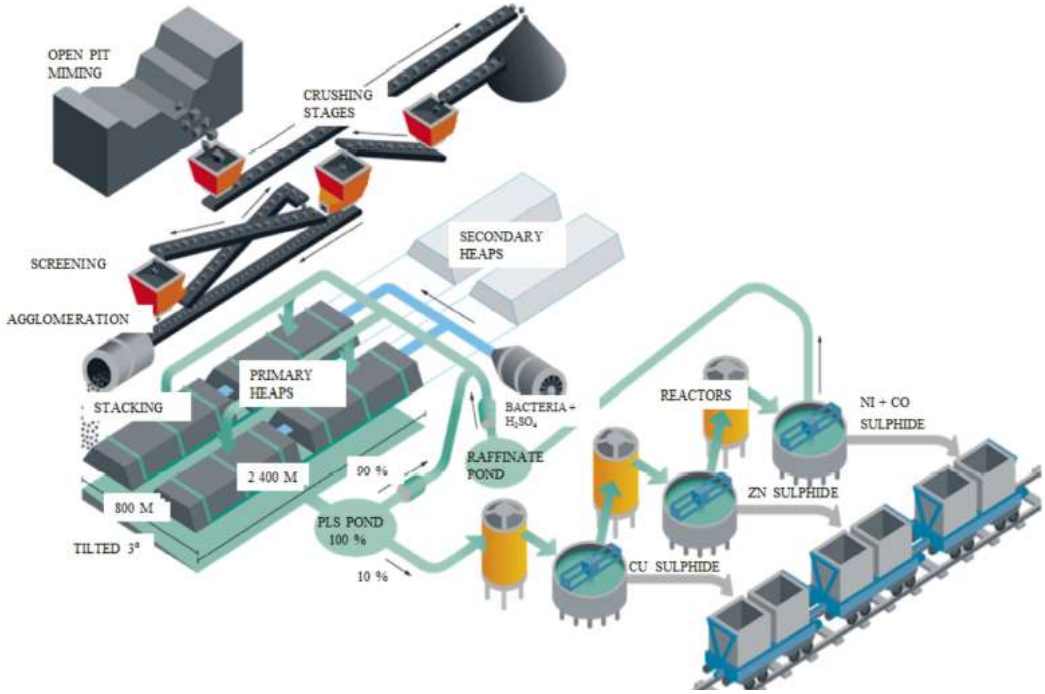

Figure 10. Overview of the Sotkamo bioleach process (Halinen, 2015).

The process produces affected water that is initially treated with alkaline precipitation, and then treated further by a reverse osmosis plant. The concentrate product is a potential source of sulphate salts. The concentrate's main ion composition is presented in Table 5.

Table 5. Ion concentrations over 1 mg/l in Sotkamo RO concentrate.

Substance	Concentration, mg/l
Ca	1460,9
Mg	55,1
Na	3609,3
K	~20
Si	1,2
SO_4	11248,7

As can be seen, Na_2SO_4 and $CaSO_4$ (gypsum) are the main expected crystallisation products. However, as was established in chapter 2.3.1, different sulphates vary in market value. Therefore, other sulphates were also considered as main products to evaluate the feasibility of EFC treatment on different cases of composition. The sulphates of sodium, potassium and magnesium were chosen as main subjects of EFC experiments.

4 Experimental procedure

This chapter describes the methods, equipment and materials used to carry out the EFC sulphate tests.

4.1 Methodology

This chapter explains the procedure of the carried out EFC experiments, starting with a description of crystalliser construction. The sulphate EFC tests were divided into two sections based on sample complexity: binary and mine water concentrate.

4.1.1 Crystalliser construction

A key part of the early experimental phase was constructing the crystalliser. As a complete crystalliser set-up was not available, the system had to be assembled out of available parts (commercial components listed in chapter 4.2). Practical knowledge of EFC was limited, so the set-up was modified and optimised during the first experimental phase. Therefore, the crystalliser set-up went through several iterative steps.

The set-up was based around a cooling compressor with coolant circulation through inlet and outlet pumps. The coolant used was a 50% mix of ethylene glycol antifreeze liquid and tap water, with freezing resistance down to -35 °C. All iterations followed one of two basic indirect cooling layouts: open or closed coolant circulation. In open circulation, the crystalliser (container that holds the sample solution) was partially submerged in coolant, which required an outer container. Closed circulation had the coolant flowing inside a coil that was placed inside the crystalliser, negating the heat transfer effects of the crystalliser material. Both circulation layouts are presented in Figure 11.

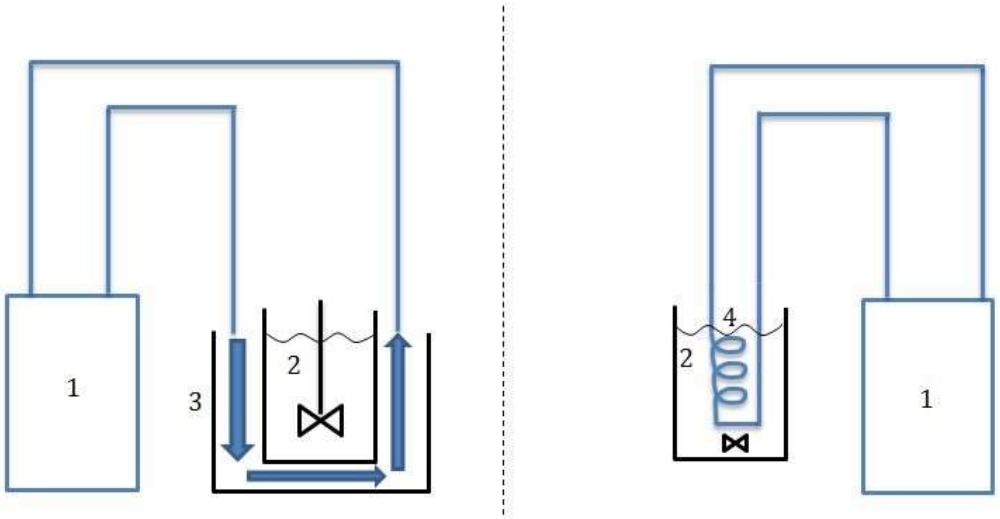

Figure 11. Used cooling layout: open cooling (left) and closed cooling (right). Numbered components are cooling compressor (1), crystalliser (2), coolant container (3) and coolant coil (4).

The initial set-up, using open circulation, included a solution container made of glass and a steel kettle as the coolant container. The solution was stirred with a mechanical mixer inserted from above. The metallic coolant container was found to be a disadvantage, as it transferred heat to the crystalliser.

The second iteration replaced the coolant container material with plastic and added outer insulation to most materials in contact with coolant to minimise heat gain. In addition, a steel crystalliser was tried to maximise heat transfer to the solution. Heavy mechanical mixing was continued. Solution cooling was found to be very effective, but significant ice scaling on the metallic heat transfer surface insulated the crystalliser. Manual removal of the ice was found to be difficult, as the ice only detached as small portions. Heavily insulating the coolant container was also found to be impractical, as it hindered sampling and observing the solution.

The third iteration used plastic as the coolant container material, with less cooling equipment insulation for easier operation. The glass crystalliser was reintroduced to the set-up. Mixing was carried out manually to gain better constant solution visibility. During cooling, ice scaling was observed, but

manual ice removal proved to be effective. As expected, the attachment of ice on glass appeared weaker than on a metallic surface. However, open coolant circulation was observed to have problems with coolant liquid balance due to limited circulation control. Therefore, closed coolant circulation was investigated as a solution to the problems.

The fourth iteration based its cooling on a hollow steel coil with closed coolant circulation. The approach made it possible to remove the outer coolant container and insulate only the glass crystalliser itself. Leaving out a strip of insulation also allowed good visibility into the crystalliser. Heat transfer was found to be very effective, as could be expected due to direct metal contact with the solution. However, space requirements of the coil limited mixing options. Magnetic stirring on the crystalliser bottom was used initially, and a mixer blade small enough to fit in the coil's centre was tested later on. The coil set-up is presented in Figure 12 and Figure 13.

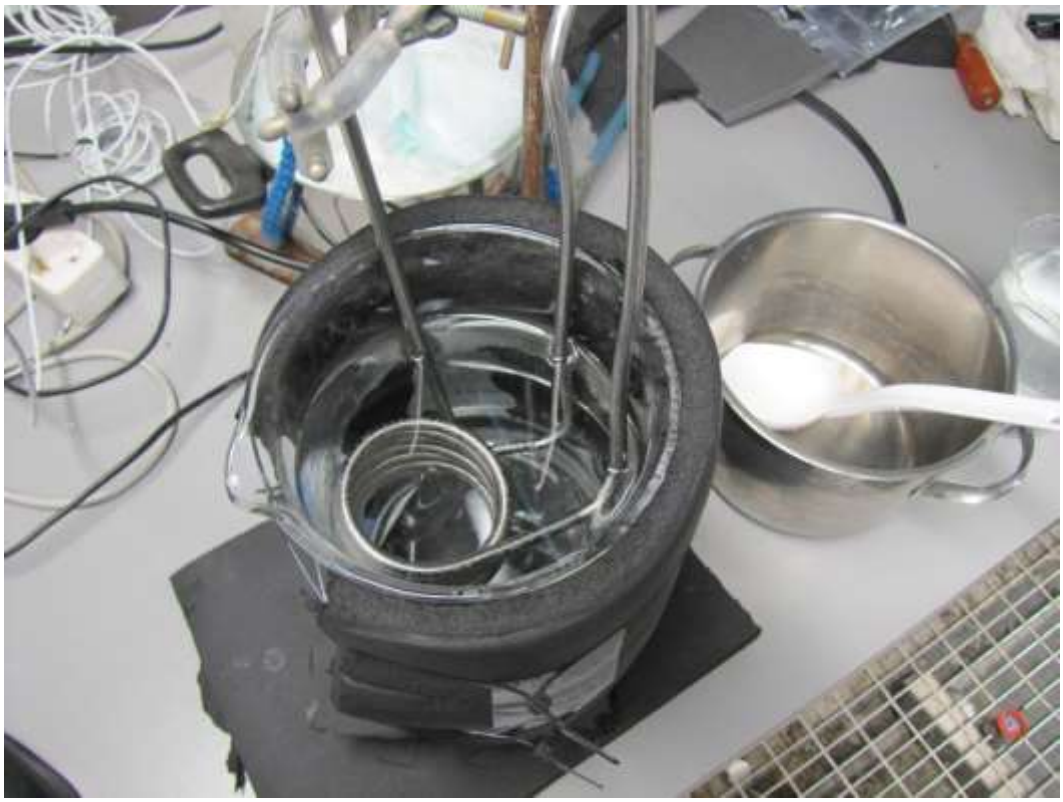

Figure 12. Fourth crystalliser iteration, using closed circulation cooling coil, crystalliser top view.

Figure 13. Fourth crystalliser iteration, using closed circulation cooling coil, with connection to cooling compressor.

Despite its advantages, the cooling coil was found to be very vulnerable to crystal scaling, which insulated most of the heat transfer surface. The problem was mostly found with ice scaling, but salt scaling was also observed with sodium sulphate. Manual removal of any scaling proved to be difficult and ineffective due to the complex surface area, and solution temperature was observed to rise from loss of heat transfer. The metallic heat transfer surface was deemed unsuitable, as post-crystallisation heat transfer would have required active scraping of scaling crystals. The scaling is pictured in Figure 14.

Figure 14. Cooling coil scaling build-up, from ice (left) and sodium sulphate (right).

The fifth and last iteration returned to using the open circulation layout due to its higher observed scaling resistance. The key parameters appeared to be the glass heat transfer surface and the option for heavier solution mixing. Coolant liquid balance problems were solved by optimising cooling compressor height relative to crystalliser, coolant tubing size and placement of tube connections to the coolant container. This set-up was found to be the best compromise between heat transfer effectiveness and scaling control. In most experiments, any scaling was feasible to remove manually. The final iteration is presented in Figure 15.

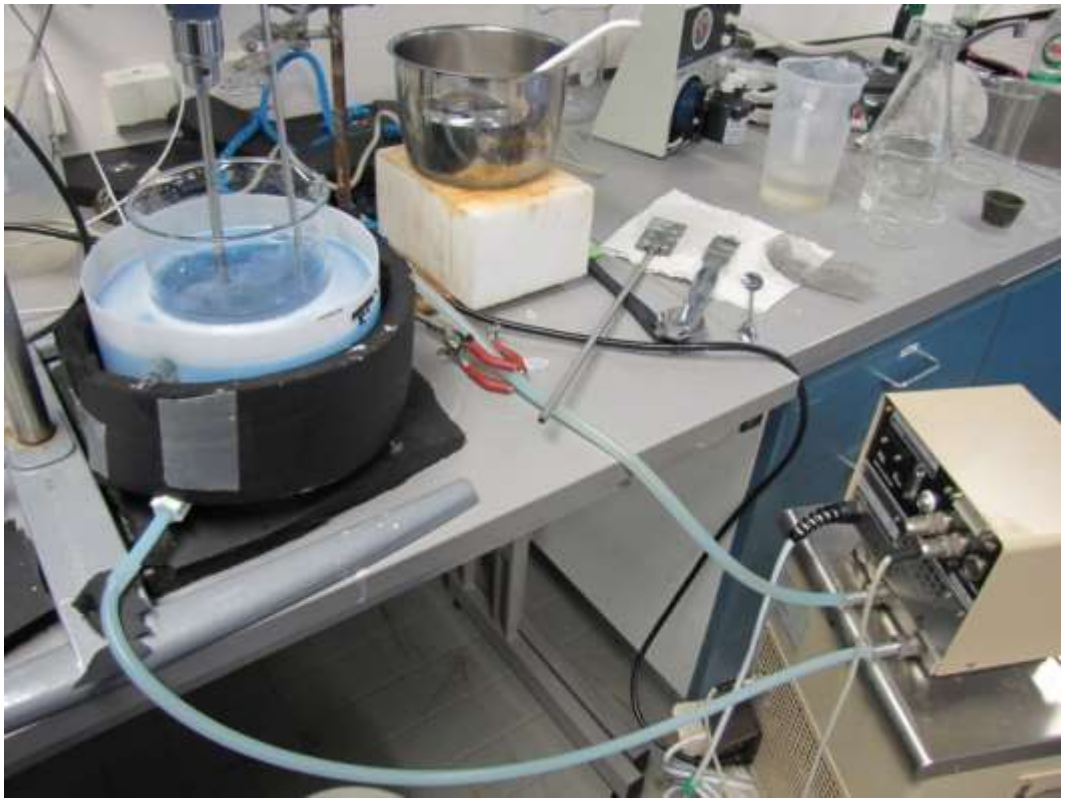

Figure 15. Fifth crystalliser iteration, with open coolant (blue liquid) circulation from cooler (right) to crystallizer (left).

As extensive crystalliser optimisation was not a primary focus of the experiments, the fifth iteration was deemed satisfactory. A combination of closed coolant circulation and a glass crystalliser container was considered, but the idea was abandoned due to lack of suitable materials. A summary of the crystalliser iterations is presented in Table 6.

Table 6. Summary of crystalliser iterations.

Iteration	Cooling	Description	Disadvantages
1	Open	Glass cryst., steel coolant kettle	High heat gain
2	Open	Steel cryst. plastic coolant kettle	Heavy ice scaling
3	Open	Glass cryst, plastic coolant kettle	Difficult coolant circulation
4	Closed	Glass cryst., metallic coolant coil	Ice scaling, test sampling
5	Open	It. 3, modified coolant tubing	Exposed coolant

4.1.2 Phase one: Binary solution EFC

The first phase of experiments focused on finding or confirming the eutectic points of the selected sulphates in water. The experiments were done using synthetic binary solutions (single salt and water) as samples. The purpose of the binary tests was to compare the crystallisation behaviour of individual salt and to establish a reference for the more complex tests. As the practical EFC experience available was limited, the tests also functioned as training for more effective operation later on. Another key part of the first experiment phase was optimising the crystalliser set-up, which was described previously.

To observe differences in cooling and crystallisation behaviour, the tests included sulphate solutions with weight ratios below, at and above the sulphates' eutectic points. All solutions were of 1,8 kg total weight to simplify calculation of weight ratios. Therefore, liquid volume of the sample depended on the amount of salt content. All tested weight fractions are presented in Table 7.

Table 7. All tested binary sulphate weight fractions.

Salt	Weight fractions tested (wt.%)				
Na_2SO_4	2	4	5	10	20
K_2SO_4	2	5	6	8	10
$MgSO_4$	18	20			

The sample of each binary test was prepared by dissolving the calculated amount of the selected sulphate salt into deionised water. The solution was heated to room temperature and magnetically stirred for at least 30 minutes to allow the solution to become homogenous. The sample was then cooled until either eutectic conditions were observed (crystallisation of both ice and salt) or the test was disrupted. Possible disruptions included low sample volume (due to ice production) or a failure of the crystallisation equipment (such as heat transfer loss). Coolant temperature was set approximately 5 °C below known or observed eutectic temperature. The solution was constantly

stirred during cooling, and stirring was kept strong enough to keep any ice moving. For mechanical stirring, rotation speed varied between 80 to 100 RPM. Due to lack of active ice scraping, ice scaling on heat transfer walls was manually detached when possible. In cases of significant ice production (in samples well below eutectic concentration), ice was removed from the crystalliser as necessary. Ice product treatment varied through tests to evaluate the effect on purity. In initial tests, ice was filtered by gravity. Later tests added vacuum filtration and drying. The final addition was washing with cooled deionised water (momentary complete submersion) combined with vacuum drying.

During each test, sample temperature was continuously measured to create a crystallisation graph, with recorded data points every 5 seconds. Conductivity was measured at intervals of roughly 5 °C. Due to equipment limits, conductivity below 1 °C could not be measured. Where possible, conductivity of the filtered eutectic solution was measured, but cases in of lengthy ice/salt separation the measurement was not done due to possible ice melting or salt dissolution. Solution samples of 2-5 ml were also taken at intervals for thermogravimetric analysis of dry substance amount, using syringe filters when solid salt presence was observed or suspected. The solution samples were spread out across the test duration to give an overview of concentration changes. Conductivity and dry substance tests were also done on ice in a selection of tests to evaluate ice product purity. Visual observations during tests included noting crystallisation events, their speed and the apparent quality of crystals.

After the cooling and stirring was stopped, the solution was allowed to settle for a few minutes, after which any salt crystals were filtered and vacuum-dried. The crystals were not washed in this phase of the experiments, as the solutions did not contain impurities. The crystals were allowed to dry overnight. The crystals and liquid samples were tested for their dry substance amount by heating them at 105 °C overnight and measuring loss of

mass to vaporisation. In earlier tests, a halogen-based fast dry substance analyser was also used, but its use was discontinued later on (based on results described in chapter 5). Dry substance analysis and temperature measurement results were used to identify the binary eutectic point of each sulphate.

4.1.3 Phase two: Mine water concentrate EFC

The second phase of experiments focused on testing EFC on multi-salt solutions, which included synthetic solutions and a sample of concentrated mine water from Sotkamo mine. Due to its high potential product value and technical viability in binary experiments, potassium sulphate was used as a base in the synthetic solutions. The solutions had a weight ratio of potassium sulphate that was higher than eutectic (9 wt.%), as the beginning of eutectic crystallisation was found to be easier to recognise when salt crystallises first. Each solution was incrementally more complex, with added cation impurities. Based on Sotkamo mine water composition, these impurities were magnesium, calcium and sodium. It should be noted that the impurity ingredients were calculated for 1,8 litres of water, but as solution weights were again a constant 1,8 kg, the actual concentrations were higher due to less water. Table 8 presents the estimated minimum and maximum impurity concentrations. Test 5's initial concentrations are presented in its respective results and discussion section.

Table 8. Minimum/maximum impurity concentrations for phase two synthetic tests (all contained 9 wt.% K_2SO_4).

Impurity	Test 1	Test 2	Test 3	Test 4	Test 5
Mg, mg/l	1400/1575	24000/27000	1400/1575	1400/1575	Mine sample
Ca, mg/l			400/450	100/113	Mine sample
Na, mg/l				1400/1575	Mine sample

Magnesium and sodium were added as $MgSO_4$ and Na_2SO_4, respectively. Calcium was added as $Ca(OH)_2$, and calcium-containing solution pH was brought below 8,00 with 1 M H_2SO_4. Initially, a calcium concentration of 700 mg/l was intended, but addition of $Ca(OH)_2$ caused the calcium to precipitate as gypsum. The addition of 400 mg/l Ca amount did not cause precipitation, but the $Ca(OH)_2$ did not dissolve completely. A dissolution of 100 mg/l was attempted for test 4 was, again, only partially successful. On analysis, test 3 solution was found to have 140 mg/l concentration of calcium, while test 4 had inconclusive results due to interference. Therefore, tests 3 and 4 represent a concentrate of relatively low calcium concentration. The actual mine sample of test 5 was concentrated up to 90% water recovery, and its calcium was precipitated as $CaCO_3$ by feeding CO_2 and increasing pH to alkaline levels. Table 9 presents the synthetic solution compositions as sulphate weight ratios.

Table 9. Phase two solution components as sulphate weight ratios.

Ingredient	Test 1 / wt.%	Test 2 / wt.%	Test 3 / wt.%	Test 4 / wt.%	Test 5
K_2SO_4	9,00	9,00	9,00	9,00	Mine sample
$MgSO_4$	0,69	11,88	0,69	0,69	Mine sample
$CaSO_4$			0,14	0,03	Mine sample
Na_2SO_4				0,43	Mine sample

The test procedure of phase two was mostly similar to the earlier tests. The solutions were cooled to reach their eutectic points, after which the eutectic conditions were maintained until the amount of ice started interfering with test handling. Conductivity, temperature and dry content amount were measured or sampled as previously. Additionally, tests 4 and 5 had an extra solution sample at their observed eutectic conditions. When cooling was stopped, salt was allowed to gravitationally separate from ice and a suitable amount of salt was vacuum filtered. The salt was washed once with deionised ice water (momentary complete submersion) and left to dry overnight. Test 4 was repeated (identical preparation) without solution sampling or product

washing to evaluate the maximum amount of eutectic salt production. In this test, as much salt as possible was separated from the solution and ice.

The air-dried salt was heated at 105 °C overnight to remove possible crystallisation water, the mass of which was measured. The dry salt product was then dissolved in deionised water for analysis. Tests 1, 2 and 3 used spectrophotometry (Hach DR 2000, method 8030) to measure Ca and Mg concentrations. The crystals and eutectic solution samples of tests 4 and 5 were analysed with ICP-OES for concentrations of Ca, Mg, Na, K, P, S, Mn, Fe, Al and Si. Test 5 also had a pre-cooling sample analysed for its initial concentrations.

4.2 Equipment and materials

The chapters below list all specific equipment and materials used in the experiments. Table 10 lists all proprietary equipment and devices used in the experiments.

Table 10. List of specific equipment used.

Function	Model name	Manufacturer
Cooler/circulator	FP-30	Julabo
Conductivity measurement	EC-300	VWR
Temperature recording circuit	NI 9205	National Instruments
Temperature circuit dock	cDAQ-9174	National Instruments
Spectrophotometer	DR/2000	Hach
Moisture analyser	HR73	Mettler Toledo
pH measurement	pH1000H	VWR
pH measurement, alternative	pH110	VWR
Mixer rotator	EURO-ST D	IKA
Vacuum pressure station	Air Cadet	Thermo Scientific
ICP-OES analyser	iCAP 7600 ICP-OES Duo	Thermo Scientific

ICP-OES analyses were carried out by Labtium Oy. Crystalliser construction used silicone tubing and insulator foam materials. Syringe filters used a 0,45

µm cellulose acetate membrane. All larger filtration was done with a Büchner funnel using a cellulose membrane with 4-7 µm sized pores. All used chemicals are listed in Table 11. Additionally, deionised water was used as solvent for all solutions.

Table 11. List of chemicals used.

Chemical	Formula	Manufacturer	Notes
Sodium sulphate	Na_2SO_4	Merck	Anhydrous
Potassium sulphate	$K2_SO_4$	Merck, VWR	Anhydrous
Magnesium sulphate	$MgSO_4*7H_2O$	VWR	Heptahydrate
Calcium hydroxide	$Ca(OH)_2$	VWR (BDH)	Anhydrous
Sulphuric Acid	H_2SO_4	(Local supply)	1 M concentration
Ethylene glycol antifreeze	Mixed	Biltema	

5 Results and discussion

This chapter presents and discusses the results of EFC sulphate experiments. It is divided between binary test results and multi-salt test results. In addition, a commercial evaluation of EFC for mine water sulphate separation is presented, based on the experiments.

5.1 Binary solution EFC

This chapter describes the results of binary EFC tests, which include experiments with sulphates of sodium, potassium and magnesium. Due to equipment optimisation, there were several non-eutectic failed tests, which are not presented here.

5.1.1 Sodium sulphate

A combination of two recorded temperature graphs for sodium sulphate is presented in Figure 16.

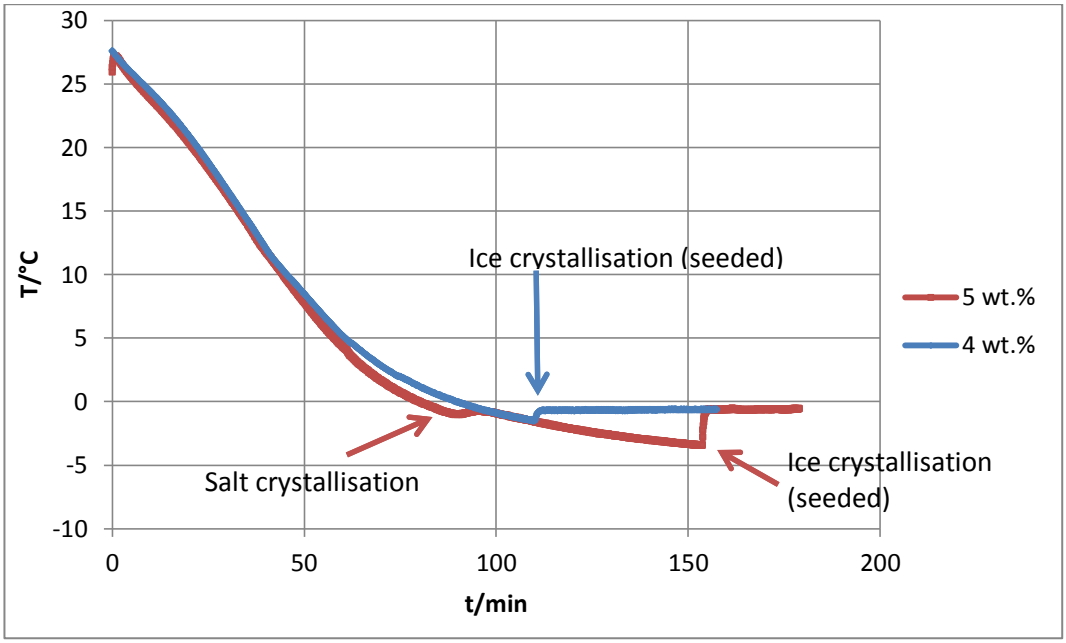

Figure 16. Temperature graphs from 4 wt.% and 5 wt.% sodium sulphate tests.

The above tests produced both salt and ice, confirming them as eutectic. As can be seen from above, the solution at 5 wt.% lead to salt crystallising first, proving the solution to be above eutectic salt content. The test was re-run later, ice melting having diluted it to around 4,4 wt.% (graph omitted for clarity). The 4 wt.% solution's salt production was minor and hard to detect, but the salt had apparently begun crystallising shortly after ice, suggesting a near-eutectic concentration. Both tests settled to an equilibrium around -0,66 °C, the apparent eutectic temperature. Dry substance amount results for the tests are presented in Figure 17. Table 12 presents conductivity results for two of the tests.

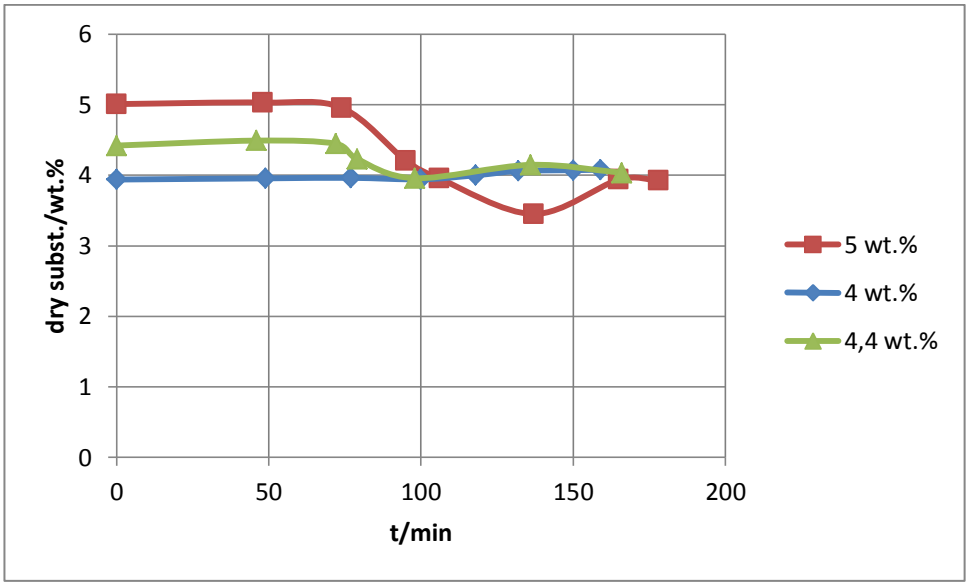

Figure 17. Solution dry substance amounts for three sodium sulphate tests.

Table 12. Sodium sulphate conductivity results for two tests.

Parameter	4 wt.%	4,4 wt.%
Initial conductivity, mS/cm	38,70	42,40
Eutectic conductivity mS/cm	39,32	39,20
Relative change %	1,60	8,16
Calculated eutectic wt.%	4,06	4,04

The dry substance analyses place the eutectic concentration between 3,9 and 4,1 wt.%, which is in agreement with the observed crystallisation behaviour. Conductivity results fall near the average. Therefore, the observed eutectic point for Na_2SO_4 was approximately -0,66 °C and 4,0 wt.%. The concentration is in agreement with literature data (Lewis, et al., 2010), but the temperature is significantly lower than the established -1,24 °C. The reason for the discrepancy could not be confirmed, but it is likely affected by the crystalliser set-up and environment, as different solutions produced very similar results. Two crystal samples of sodium sulphate are pictured in Figure 18.

Figure 18. Two samples of EFC sodium sulphate product.

The left crystal sample was found to have dry substance amount of 44,6 %, very close to the 44,1 % of $Na_2SO_4*10H_2O$. The right one had less water at 52,5 %, close to an equivalent of $Na_2SO_4*7H_2O$. However, it should be noted that during drying, the right sample appeared to lose much of its crystal size. Therefore, the sulphate may have lost some of its initial crystallisation water, which is possible as phase data predicts the decahydrate to be dominant in eutectic conditions. Sodium sulphate crystals were generally found to be somewhat difficult to separate from ice, as they tended to form a slurry-like mix. In solution, the crystals resembled small, transparent needles.

5.1.2 Potassium sulphate

Temperature graphs of three potassium sulphate tests at different concentrations are presented in Figure 19.

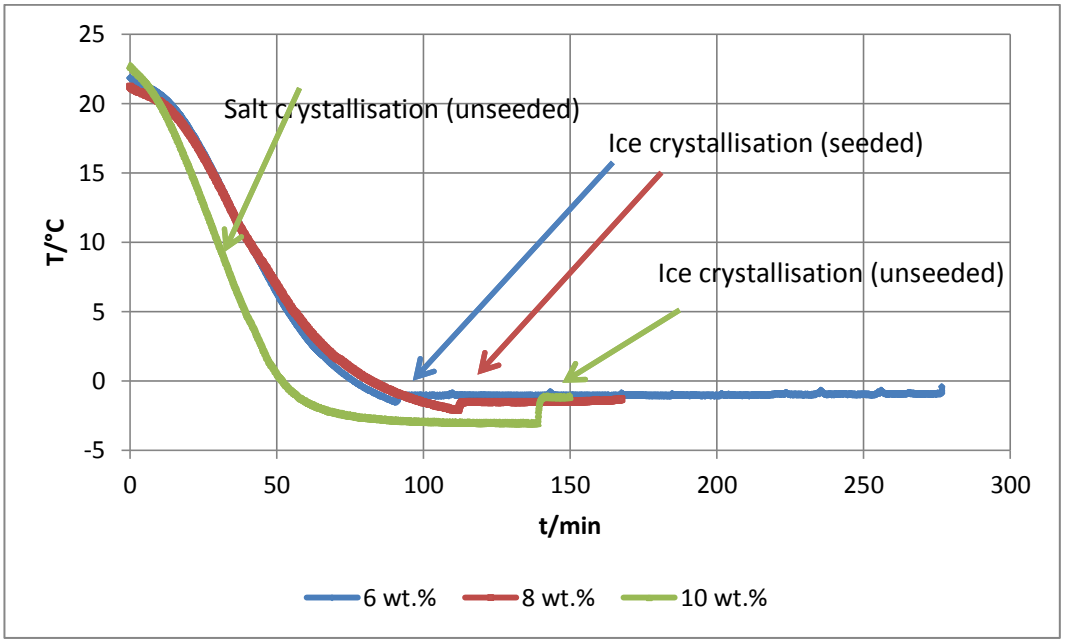

Figure 19. Temperature graphs of two K_2SO_4 EFC tests. Note: 10 wt.% test was on a different cooling iteration.

All tests in Figure 19 reached double crystallisation, and therefore were eutectic. However, it was observed that K_2SO_4 salt crystallisation was very subtle and could not be identified from temperature information, possibly due to endothermic nature. Eutectic temperature seemed to vary between -1,1 °C and -1,5 °C. Dry substance analysis and conductivity results are presented in Figure 20 and Table 13, respectively.

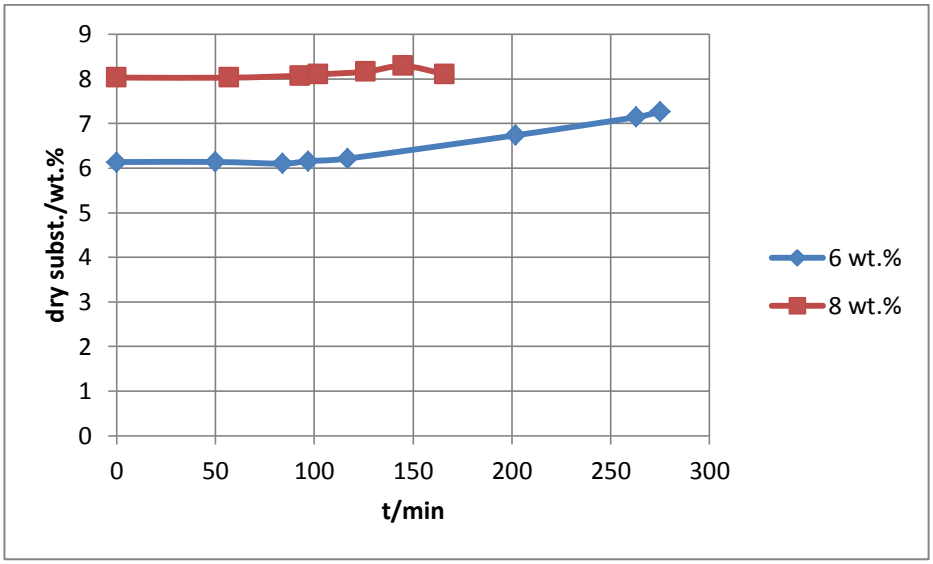

Figure 20. Two potassium sulphate EFC test dry substance analysis results. 10 wt.% test was omitted due to poor performance of the halogen fast analyser, which was discarded from analyses.

Table 13. Potassium sulphate EFC tests' conductivity results.

	6 wt.%	8 wt.%	10 wt.%
Initial conductivity, mS/cm	63,50	82,50	97,30
Eutectic conductivity, mS/cm	75,40	80,00	73,00
Relative change %	18,74	3,13	33,29
Calculated eutectic wt.%	7,12	7,76	7,50

Again, there is some variance in the results, but eutectic concentration appears to fall between 7-8 wt.%. Therefore, the observed eutectic point is approximately -1,3 °C and 7,5 wt.%. Phase literature was not available, so the result cannot be confirmed. Still, K_2SO_4 appears to have colder and more concentrated eutectic conditions than Na_2SO_4. Two samples of EFC-produced crystals are presented in Figure 21.

Figure 21. Potassium sulphate crystal products.

Overall, the crystals appeared very powder-like, suggesting little to no crystallisation water. Dry substance analysis for the above crystals gave results of 100,00 % (left) and 99,43 % (right). The binary EFC product of potassium sulphate was therefore assumed to be pure anhydrous K_2SO_4. In the solution, the crystals separated from ice relatively easily and did not form a slurry at all. In solution, the crystals were very small and opaque.

5.1.3 Magnesium sulphate

Due to higher cooling requirements and equipment limitations, magnesium sulphate had the least amount of successful eutectic tests. Temperature graph for the most successful test is presented in Figure 22.

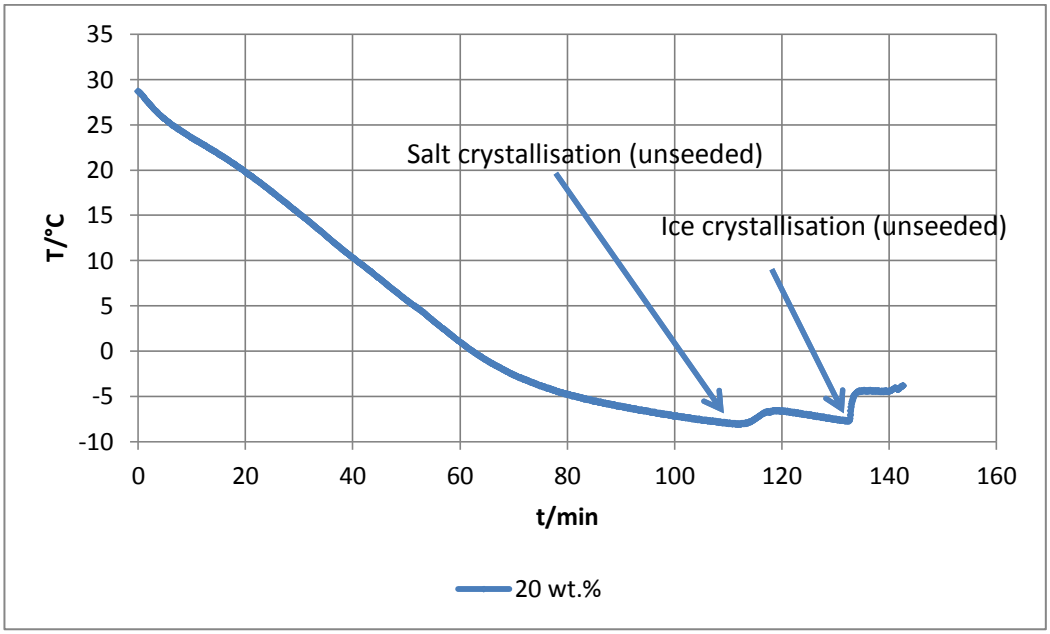

Figure 22. Temperature graph for 20 wt.% $MgSO_4$ test.

The high solubility of the sulphate is seen in the low temperature of -8 °C that was required for initial salt crystallisation. After ice crystallisation, temperature appeared to stabilize between -4,4 °C and -3,8 °C, rising towards the end. As salt crystallised first, 20 wt.% was confirmed to be above eutectic concentration. Dry substance analysis results are presented in Figure 23.

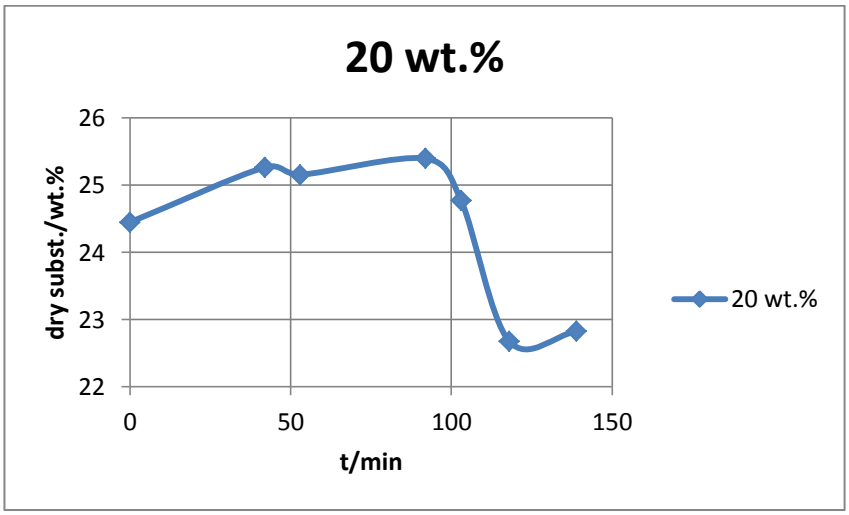

Figure 23. Dry substance analysis results for $MgSO_4$.

The results indicate that 105 °C was not sufficient to remove all crystallisation water from $MgSO_4$, as there appears to be both systematic and

random error (initial value higher than actual solution concentration). However, a major decrease in concentration seems to correlate with the temperature graph, mirroring salt crystallisation. If an average of pre-crystallisation values is compared with the final value, a 9,82 % decrease is gained. When applied to the actual initial concentration of 19,92 wt.%, an eutectic concentration of 18,15 wt.% is gained. Himawan et al. (2006) found $MgSO_4$ to be eutectic at 18 wt.%, which would be in agreement with the value here. Previously established value for eutectic temperature is -3,9 °C, which falls within the observed stable range. The crystal product is pictured in Figure 24.

Figure 24. Magnesium sulphate crystal product.

Crystal dry substance amount was found to be 58,00 %. The value resembles the 57,20 % of $MgSO_4*5H_2O$, but the result is likely to be inaccurate. After heating, the crystals still appeared to have residual crystallisation water, and complete water removal was unsuccessful in previous similar tests. One possibility is that the salt crystallised as the expected $MgSO_4*12H_2O$, and dehydrated to the stable $MgSO_4*7H_2O$, which would have a water loss of 57,18 %. However, the exact amount of crystallisation water could not be confirmed. In solution, the crystals appeared as large, transparent needles that formed slurry and were difficult to separate from ice effectively. The results show that magnesium sulphate has significantly different eutectic

behaviour than the other sulphates, correlating with its greatly higher solubility.

5.1.4 Binary EFC summary

From the binary test results, potassium sulphate appears to be promising for further study. The salt does not require a significantly lower crystallisation temperature than sodium sulphate, and it contains no crystallisation water. In addition, K_2SO_4 crystallisation seems endothermic or very temperature neutral, likely due to anhydrous nature, which puts less strain on cooling. As seen in chapter 2.3.1, potassium sulphate has the best average market price of all tested sulphates. To evaluate an economically optimal case, K_2SO_4 was decided to be the base eutectic salt for the multi-salt synthetic tests.

5.2 Mine water concentrate EFC

These chapters present the results of the multi-salt tests that included potassium-based synthetic solutions and a sodium-based mine water concentrate sample.

5.2.1 Mg as impurity

The temperature graphs of the two tested Mg impurity concentrations (actual values) are presented in Figure 25.

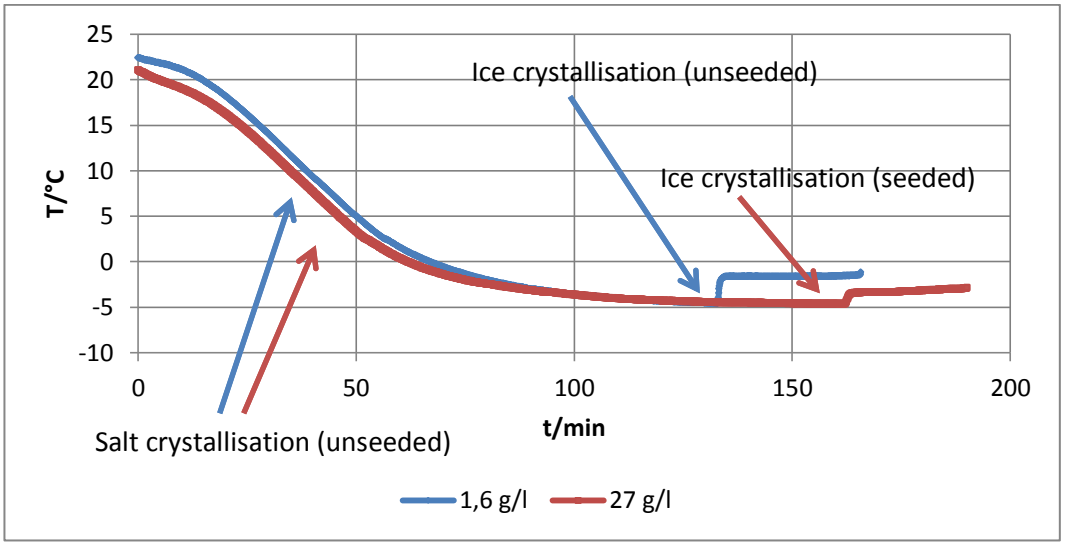

Figure 25. Temperature graph for the two tested Mg impurity concentrations.

The lower Mg concentration solution was found to be eutectic around -1,6 °C, and the higher concentration one roughly at -3,2 °C. However, the latter was observed to steadily increase, which could mean a higher true equilibrium temperature. In both cases, the added magnesium clearly decreased the eutectic temperature, which is an expected effect for impurity additions. Both salt crystallisations appeared endothermic and subtle, as it was with K_2SO_4. Dry substance analysis results for both impurity amounts are presented in Figure 26, and the crystal products are pictured in Figure 27.

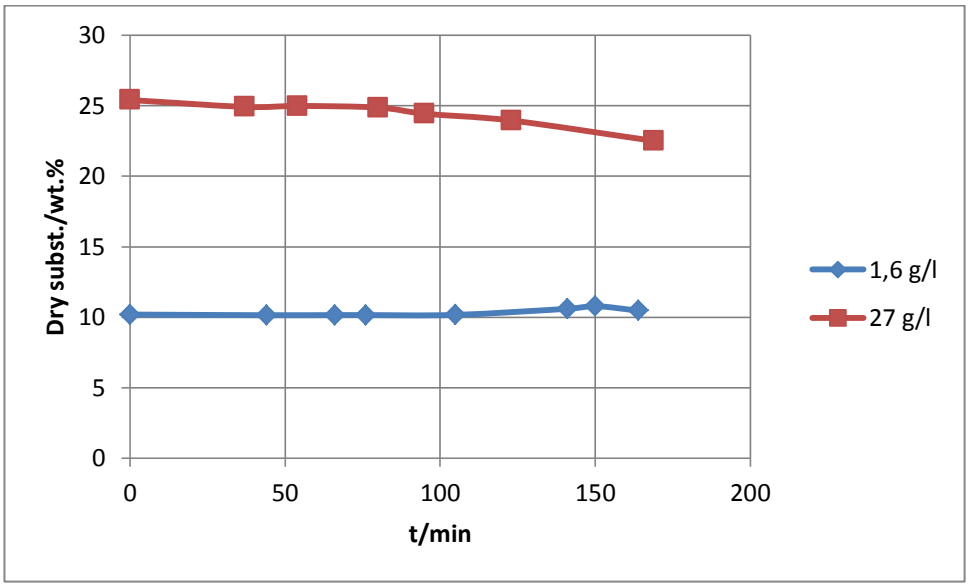

Figure 26. Dry substance analysis results, Mg as two impurity concentrations.

Figure 27. Crystal products for K2SO4 with Mg impurities, 1,6 g/l (left) and 27 g/l (right)

The lower Mg-impurity crystals resembled K_2SO_4 both by dry appearance and by behaviour in solution. The crystals were found to have no crystallisation water (100 % dry substance amount). Magnesium content was found to be 0,05 wt.%, which was assumed to be a solution leftover since the crystals were only washed once. Therefore, the eutectic crystallisation product was likely to be very pure K_2SO_4.

The higher Mg-impurity crystals appeared to have small reflective surfaces, which previously had been a result of crystallisation water. Dry substance amount was found to be 76,44 wt.%, which is similar to $MgSO_4*2H_2O$ (76,96 wt.%) and $K_2SO_4*MgSO_4*6H_2O$ (73,16 wt.%). Magnesium amount was found to be 6,96 wt.% which is closest to $K_2SO_4*MgSO_4*6H_2O$ (6,04 wt.%). Due to the mixed appearance of the salt, some deviation in precise composition was expected. Therefore, the salt was likely $K_2SO_4*MgSO_4*6H_2O$, or Schönite. Due to these results, the following multi-salt tests were based on the lower magnesium concentration, as it seemed to enable selective crystallisation of K_2SO_4.

5.2.2 Mg and Ca as impurities

The EFC temperature graph for potassium sulphate with Mg and Ca impurities is presented in Figure 28. 18 ml of 1 M H_2SO_4 was used to

neutralise the solution, which caused minor dilution. In addition, the gypsum precipitation and filtration described in chapter 4.1.3 also affected the solution. Final Mg and Ca concentrations were found to be 1,0 g/l and 0,14 g/l, respectively.

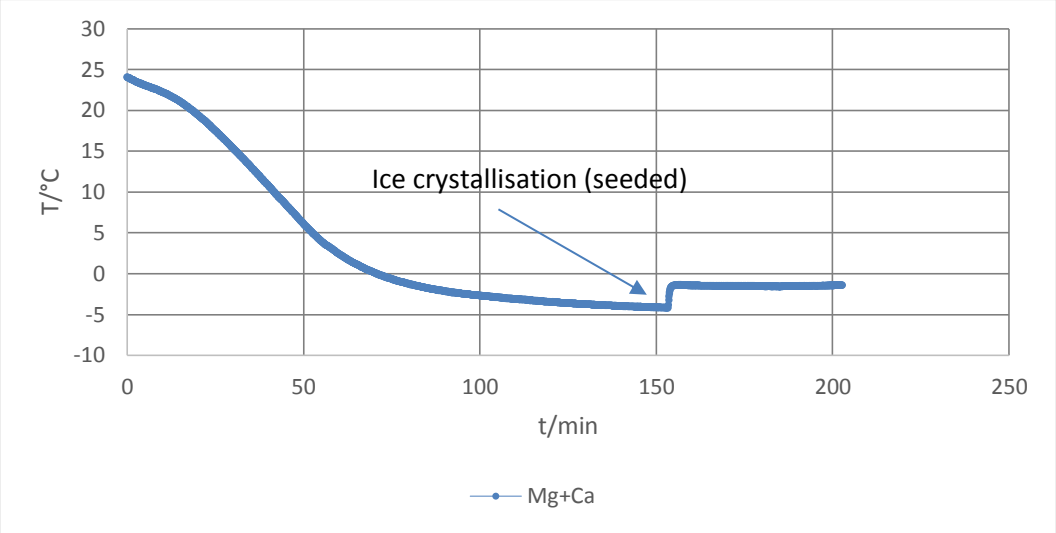

Figure 28. Temperature graph for K2SO4 solution with Mg and Ca impurities.

The test produced much of the same behaviour seen in the 1,6 g/l Mg-impurity test. Eutectic temperature appeared to settle at -1,50 °C, which is slightly lower than without calcium. However, due to the aforementioned extra dilution, the difference was expected. Dry substance analysis results are presented in Figure 29, and the crystal product is pictured in Figure 30.

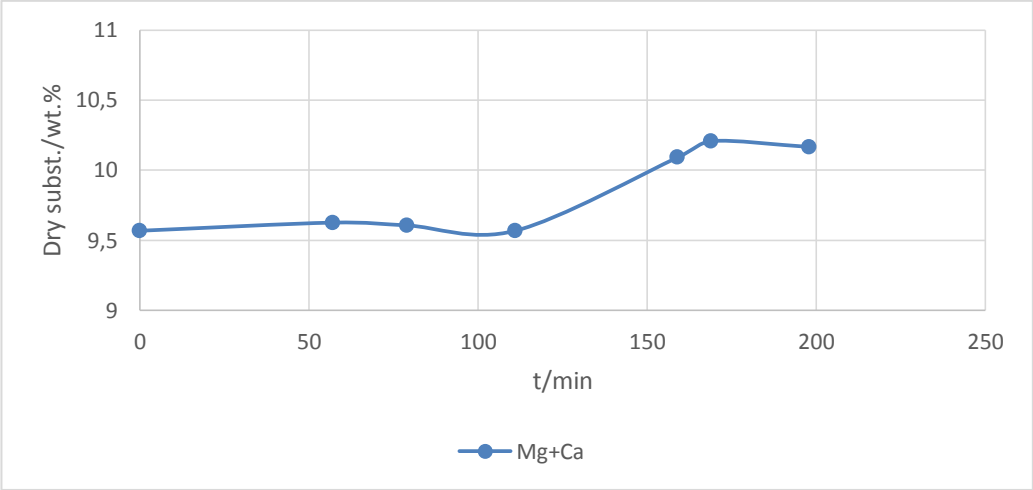

Figure 29. Dry substance analysis results for potassium sulphate solution with Mg and Ca impurities.

Figure 30. Crystal product of potassium sulphate solution with Mg and Ca impurities.

Dry substance analysis confirms the slight initial dilution, and the eutectic value is similar to the test without calcium. The crystals were found to contain 99,95 wt.% dry substance, which indicates little to no crystallisation water. Crystal appearance and behaviour was similar to K_2SO_4. Crystal analysis found there to be 0,07 wt.% of Mg and 0,61 wt.% of Ca. The values are relatively low, but calcium is present in higher amount than what its solution concentration suggests. Small amounts of gypsum may have crystallised at some point before washing, possibly during filtration. In that case, washing may have had a concentrating effect, as small amounts of the crystal product dissolved during washing. Any gypsum might have dissolved in a smaller ratio than K_2SO_4, resulting in higher weight fraction of Ca. However, the effect was not confirmed.

5.2.3 Mg, Ca and Na as impurities

The EFC temperature graph for potassium sulphate with Mg, Ca and Na impurities is presented Figure 31. The actual impurity values were approximately 1,6 g/l for Mg and Na. Due to spectrophotometer interference, initial Ca concentration could not be confirmed, but it was estimated to be around 0,05 g/l, assuming 50 % dissolution. 5 ml of 1 M H_2SO_4 was used to neutralise the solution, bringing the pH to 4,80.

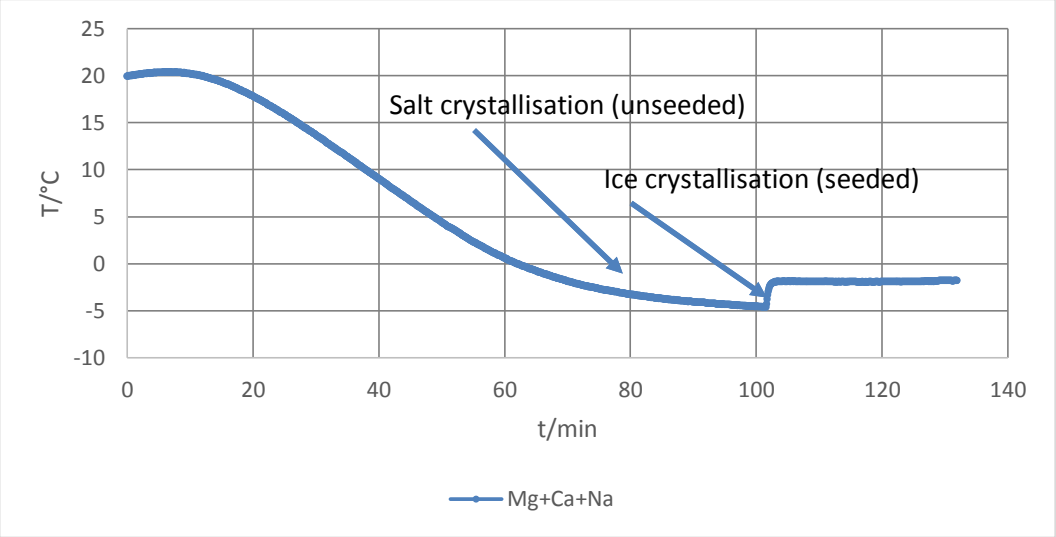

Figure 31. Temperature graph for K_2SO_4 solution with Mg, Ca and Na impurities.

Crystallisation behaviour was not observed to have major changes, but the eutectic temperature decreased to around -1,90 °C. The change was an expected effect of sodium addition, as the same mass of magnesium had decreased the temperature in earlier tests. No other significant differences were noted from temperature data. The initial salt crystallisation was very minor, seen as few barely visible individual crystals. Dry substance analysis results are presented in Figure 32 and ICP-OES results of a eutectic sample in Table 14.

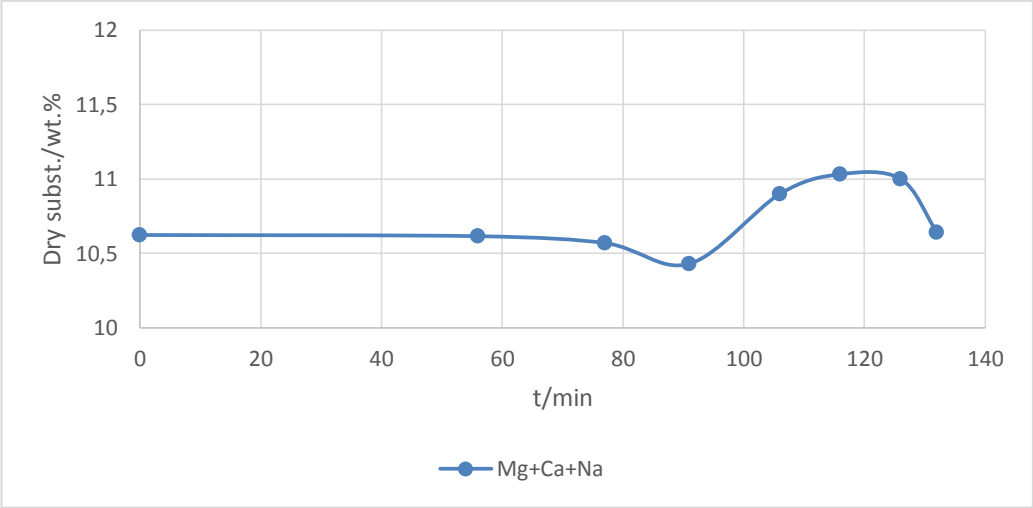

Figure 32. Dry substance analysis results of potassium sulphate solution with Mg, Ca and Na impurities.

Table 14. ICP-OES results over 0,1 mg/l of a eutectic sample of K_2SO_4 solution with Mg, Ca and Na impurities.

Element	Ca	Mg	Na	K	P	S
Eutectic mg/l	98	1800	1700	44000	7,8	22000

Given that, the original concentration of K was approximately 47000 mg/l, there was a 6,81 % decrease in concentration. If applied to the actual initial fraction of K_2SO_4, 9,32 wt.%, a eutectic value of 8,73 wt.% is gained. The value is higher than in binary tests, and in conflict with dry substance analysis. It is possible that the previously observed difficulty in removing $MgSO_4$ crystallisation water is interfering with related results. The crystal product is pictured in Figure 33, and crystal contents gained from ICP-OES results are presented in Table 15.

Figure 33. Crystal product of K2SO4 solution with Mg, Ca and Na impurities.

Table 15. Crystal elemental contents gained from ICP-OES results, K2SO4 with Mg, Ca and Na impurities.

Element	Ca	Mg	Na	K	P	S
In crystals, wt.%	0,032	0,010	0,112	41,328	0,009	17,331

The crystals were found to contain 99,92 wt.% of dry substance, indicating little to no crystallisation water. The amount of K and S in the crystals closely mirrors the values in pure K_2SO_4, 44,88 w.t% and 18,40 wt.%, respectively. All impurities make up 0,16 wt.% of the crystals, which translates to 99,84 % purity as potassium sulphate. Therefore, good selectivity for K_2SO_4 can be maintained in the presence of several elements of impurity. An identical second test run of the solution yielded 20,437 g of eutectic salt product during 36 minutes of eutectic conditions. As pre-eutectic crystallisation was minor and small amounts of salt were lost to transfer, the result was assumed representative for this test.

5.2.4 Mine water concentrate

The initial concentrations (by ICP-OES) of the mine water concentrate are presented in Table 16. The temperature graph for the concentrate's EFC test is presented in Figure 34.

Table 16. ICP-OES results of initial concentrations for mine water concentrate sample.

Element	Ca	Mg	Na	K	P	S	Al	Si
Initial mg/l	100	76	16300	390	1,7	11700	0,43	26

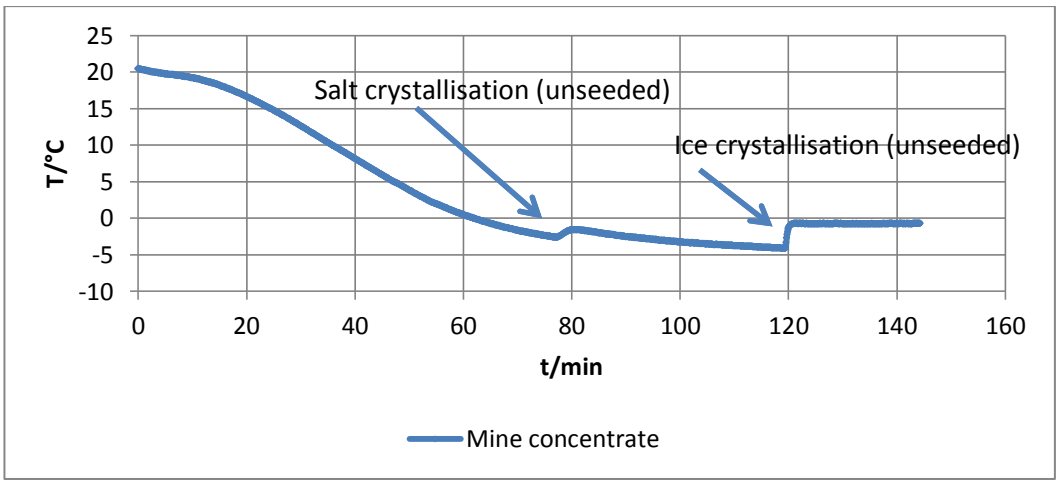

Figure 34. EFC temperature graph for mine water concentrate.

The concentrate behaved very similarly to the synthetic tests in the way that the main salt's (here sodium sulphate) eutectic point was decreased. Here, eutectic temperature is approximately -0,77 °C. The test also seems to confirm that the earlier discrepancy from literature value for Na_2SO_4 eutectic temperature is systematic and is likely caused by the equipment. Otherwise, the concentrate behaved like Na_2SO_4 above eutectic concentration, with a clearly exothermic first crystallisation of salt. Dry substance analysis results for the test are presented in Figure 35, and ICP-OES results for a eutectic sample in Table 17.

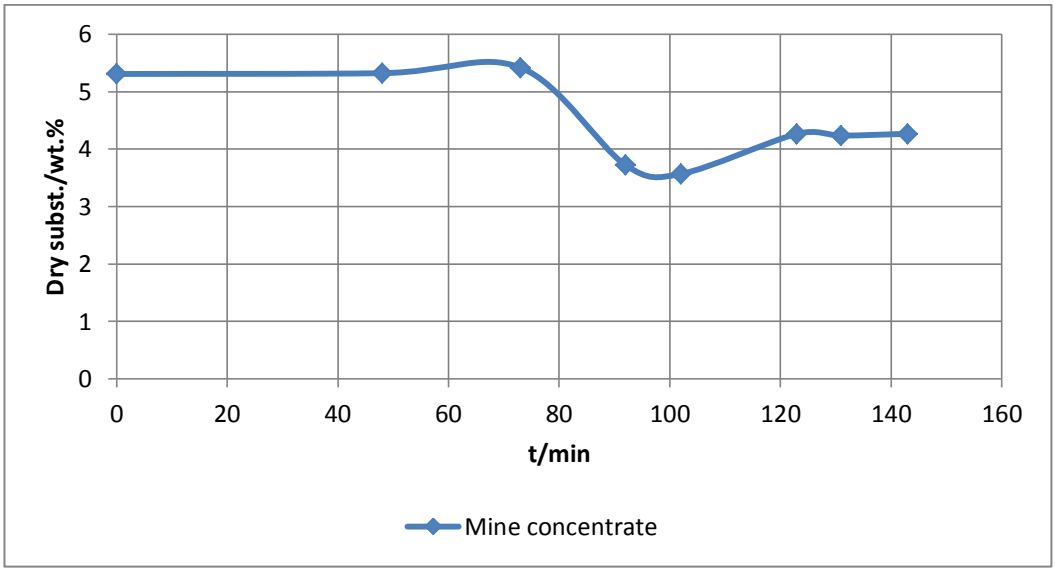

Figure 35. Dry substance analysis results for mine concentrate test.

Table 17. Eutectic ICP-OES results for mine concentrate test.

Element	Ca	Mg	Na	K	P	S	Si
Eutectic mg/l	142	98	13200	440	2,4	9400	46

Calculated from Table 16, the initial ratio of Na_2SO_4 was approximately 4,93 wt.%. Since the overall dry substance amount changed 24,42 %, the eutectic ratio for Na_2SO_4 here would be 3,96 wt.%, which is in good agreement with literature and previous tests. The relatively low amount of magnesium detected is likely to be not enough to cause the water removal problems seen in synthetic solution tests. Additionally, the much higher impurity levels in the synthetic solutions may have had an effect on eutectic concentration that was not observed in this test. The crystal product of the mine concentrate is pictured in Figure 36, and the crystals' ICP-OES results are presented in Table 18.

Figure 36. Crystal product of mine concentrate.

Table 18. Crystal elemental ratios based on ICP-OES results.

Element	Ca	Mg	Na	K	P	S	Si
In crystals, wt.%	0,02	<0,01	29,23	0,06	0,02	21,53	<0,01

The ratios of Na and S are close to theoretical ones of Na_2SO_4, 32,37 wt.% (Na) and 22,57 wt.% (S). Eliminating the impurities from 100 % would give 99,89 % pure Na_2SO_4. The crystals contained 84,27 wt.% dry substance, which would be between one and two units of crystallisation water for Na_2SO_4. Like in previous sodium sulphate tests, the product appeared to lose some crystallisation water when drying, so it is likely that initial crystallisation contained more water than measured here. In solution, the crystals appeared as small, transparent needles. Overall, impurities of the mining process did not appear to significantly affect the crystallisation of sodium sulphate. The main difference to the single-salt solution was the lower eutectic temperature, which was an expected effect.

5.3 Ice purity

A collection of test results (spanning both phases) on ice purity is presented in Table 19.

Table 19. Results on tests on eutectic ice.

Washing method	Vacuum drying	Light wash + vacuum	Submersed once + vacuum
Dry salt in solution, wt.%	2,01	8,07	8,46
Dry salt in ice, wt.%	1,13	2,54	0,23
Ice /solution content, wt.%	56,14	31,47	2,74
Ice purity, wt.%	98,87	97,46	99,77

The results indicate that the washing method and amount have a major impact on ice purity. Sufficient washing appears to be able to remove almost all impurities from ice. Since washing was limited to one time here, it is possible that very high ice purity can be attained with further or more thorough washing. As potable water has been produced in previous EFC studies, it is very likely to be possible with the solutions tested here.

5.4 Economical evaluation

Due to the massive capacity difference between the tested experimental scale and the case mine process, a simplified theoretical estimate was used for evaluating the process economy. Two feed cases were considered: a current actual RO concentrate (67,7% water recovery) and a potassium-based feed that was more concentrated (90,0% water recovery). The latter feed used higher water recovery to account for potassium sulphate's higher eutectic concentration, as was done in the experimental phase. A pre-concentration volume of 600 m^3/h was used, resulting in feed volumes of 193,7 m^3/h (sodium concentrate) and 60,0 m^3/h (potassium concentrate). The evaluation assumed a steady state single step process with complete separation of main salt product and 90 % water recovery as ice.

The first energy requirement considered was cooling the feed to eutectic temperature. For this stage, initial feed temperature was assumed to be 20 °C. The final temperature was chosen as -1,5 °C for the sodium-based feed

and -2,0 °C for the potassium-based feed (based on eutectic temperatures). The feeds' specific heat was approximated as 4,0 kJ/(kg*K), roughly the average value for water in this area (Keskinen, 2015). The following equation was used for the initial cooling energy:

$$E_{cooling} = \Delta T * C_p * \frac{m*1000}{3600s} \quad (1)$$

where ΔT is temperature difference

C_p is specific heat

and is feed mass stream (assumed to equal volume here)

The results using equation (1) are presented in Table 20.

Table 20. Cooling energy requirements for the chosen feeds.

Parameter	Feed: 67% WR Na	Feed: 90% WR K
Feed volume, m^3/h	193,6	60,0
Cooling energy, kWh	4625,7	1466,7

The next consideration was the energy required to crystallise both ice and salt. The following equation was used:

$$E_{cryst} = \Delta H_{fus} * \frac{m_{solid}}{3600s} \quad (2)$$

where ΔH_{fus} is the heat of fusion (or heat of crystallisation)

and m_{solid} is the mass stream of ice or salt

For ice, a heat of fusion of 333,6 kJ/kg was used, and for the salts, heats of crystallisation of 242,9 kJ/kg ($Na_2SO_4*10H_2O$) and 136,6 kJ/kg (K_2SO_4) were used (Haynes, 2015). Sulphate amount used the cation as the limiting factor. Pre-concentration amount of sodium in the case process (sodium feed) was 1164,8 mg/l. An equimolar amount of 1980,9 mg/l was used for the potassium feed, taking into account the higher molar mass of potassium.

The crystallisation and total energy results using equation (2) are presented in Table 21.

Table 21. Crystallisation and total energy requirements for the chosen feeds.

Parameter	Feed: 67% WR Na	Feed: 90% WR K
Salt content, kg/h	4897,2	2648,5
Ice content, kg/h	169864,3	51616,3
Salt energy req., kWh	330,4	100,5
Ice energy req., kWh	15740,8	4783,1
Cooling energy, kWh	4625,7	1466,7
Total req. energy, kWh	20696,9	6350,3

For the final operation costs, conversion into electrical energy was done by assuming a cooling compressor with a coefficient of performance (COP) of 4. The high value was chosen to represent the possibility of using the natural cooling power of boreal conditions present in the case process. The electrical requirement was increased by 15% to approximate the needs of auxiliary equipment such as pumps and separators. For price of electricity, 0,05

€/kWh was used. The calculated operational costs and income are presented in Table 22.

Table 22. Calculated costs and income for the chosen feeds.

Parameter	Feed: 67% WR Na	Feed: 90% WR K
Req. Electicity, kWh	5950,4	1825,7
Salt production cost, €/ton	60,8	34,5
Anhydrous cost, €/ton	137,8	34,5
Feed treatment cost, €/ton	1,54	1,52
Salt yield, t/a	18912,5	23201,2
Operational costs, M€/a	2,61	0,80
Salt sale income, M€/a	-1,15	10,46

The results indicate that the current Na-based RO concentrate is not profitable to treat with EFC. Significant factors in the results are salt yield and sale price. The more concentrated feed using the more valuable potassium sulphate appears profitable. It should be noted that the evaluation is purely electricity-based and does not take into account all the sources of operational costs, nor the different total chemistry costs of the hypothetical K-based feed. However, it also assumes a simple EFC process without efficiency-increasing engineering such as heat recovery and multiple crystallisation steps.

In his more in-depth analysis of the economy of an EFC process that incorporated all required equipment and resources, Vaessen (2003) gained the results presented in Table 23.

Table 23. Economy of a KNO3-producing EFC process (Vaessen, 2003).

Main salt	KNO3
Feed, t/a	150000
Salt in feed, wt.%	15
Salt produced, t/a	21475
Costs, M€/a	1,25
Salt cost, €/ton	58,2
Feed treatment cost, €/ton	8,3
Total investment, M€	7,133

Anhydrous salt production costs appear similar, but the higher cost per ton of feed may be more realistic. Vaessen's investment value was used as a reference for estimating the capital cost of an EFC process that is based on the 60 t/h potassium-based feed. Capital cost estimation used the following equation:

$$C_2 = C_1 \frac{I_2}{I_1} \left(\frac{S_2}{S_1}\right)^R \quad (3)$$

where C is a capital cost,

S is a capacity,

I is an inflation index,

and R is the scale-up exponent.

For the R exponent, Remer & Chai (1993) presented a value of 0,65 for affected water demineralisation process plants. The value of 0,70 was used to compensate for the lack of large scale EFC applications. For the inflation indices, Chemical Engineering Plant Cost Index (CEPCI) annual values for 2003 and 2016 were used. Feed mass was used as capacity. With equation (3), the cost estimate for the potassium-based feed process was:

$$C_2 = 7{,}13\ M€ * \frac{541{,}7}{402{,}0} * \left(\frac{60\frac{t}{h}}{20\frac{t}{h}}\right)^{0{,}70} = 20{,}74\ M€$$

The value is a rough estimate, as it is not calculated by the specific needs of the process. The cost should reflect the order of investment magnitude required, and it is worthy to note that an EFC process of this size has not been applied to date. For a truer investment evaluation, a full-scale process layout should be planned and used as a calculation base.

To evaluate the cost sensitivity of the hypothetical K-based feed, the impact of increased costs and decreased salt prices on the payback period was calculated. The results are presented in Figure 37 and Figure 38 .

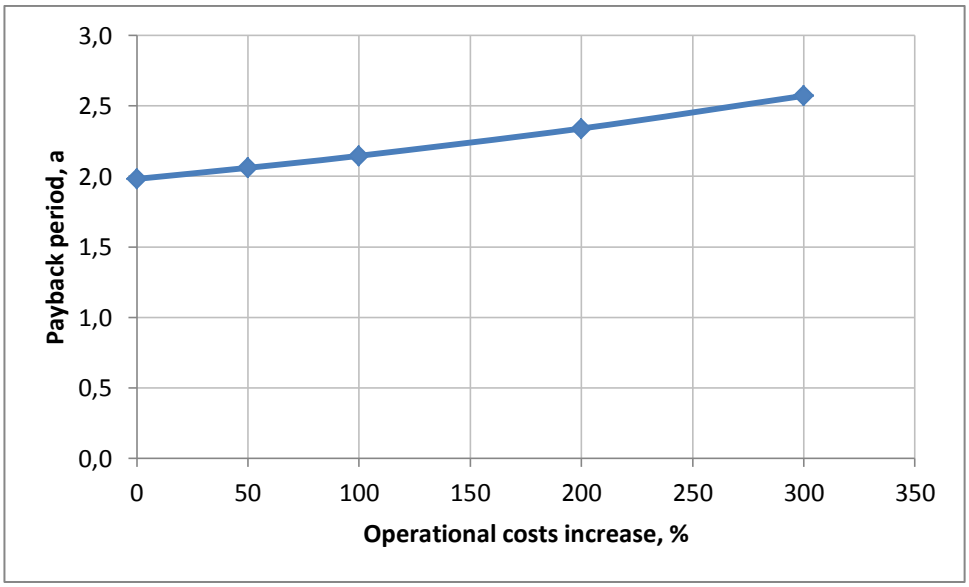

Figure 37. Impact of increased operational costs on payback period.

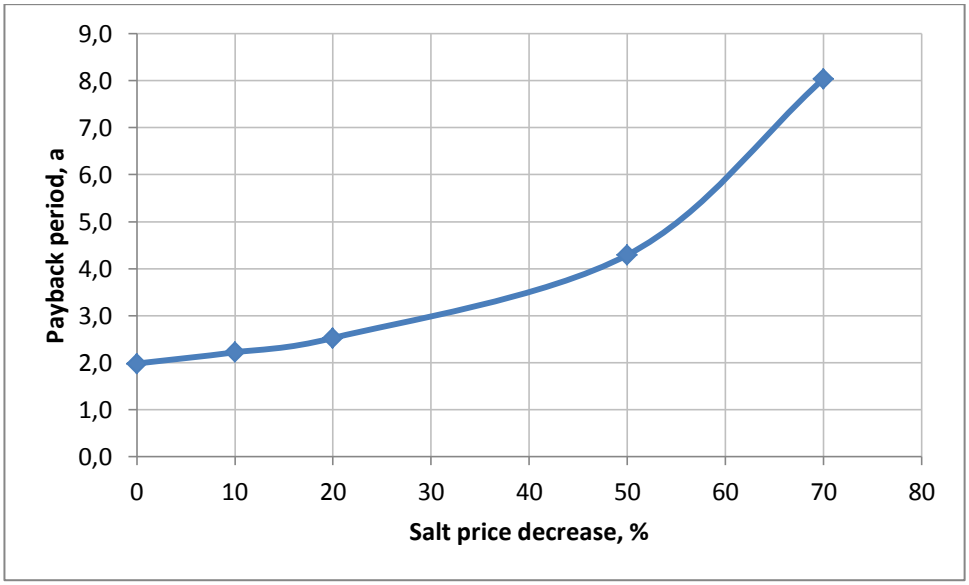

Figure 38. Impact of decreased salt sale price on payback period.

The results show that the K_2SO_4-producing EFC process is resistant to increases in operational costs, mostly due to the low costs relative to salt sale price. Fluctuations in salt price have a clearly higher impact, with a 50%

increase more than doubling the payback period. It should be noted that all financial results are before taxes. The hypothetical process seems to conform to established EFC qualities of high investment costs but low operational expenses.

6 Conclusions

Applying EFC to single-salt solutions was mostly successful and predictable. All tested sulphates had their individual crystallisation areas, and the sulphates' differences in solubility translated to differences in eutectic behaviour. Sodium sulphate's eutectic temperature consistently differed from established literature data, which was assumed to be an effect of the cooling equipment and environment. Magnesium sulphate, on the other hand, reflected literature data well. Despite lack of literature phase data, potassium sulphate behaved according to the expectation based on solubility, with a eutectic temperature close to sodium sulphate's literature value. Potassium sulphate was unique in its anhydrous crystallisation, while sulphates of sodium and magnesium had significant amounts of crystallisation water in their structure. Presence of crystallisation water appeared to be the greatest factor in crystallisation behaviour and crystal size, and it appeared to cause clearly exothermic crystallisation.

In multi-salt tests, EFC's selectivity proved to be sufficient, as K_2SO_4 crystallised with high purity in the presence of several impurities. Additional ions dissolved decreased eutectic temperature, which was consistent with the literature data on multi-salt solutions. A minimum of -2,0 °C eutectic temperature for K_2SO_4 was reached. In low enough amounts, the impurities did not seem to be crystallised with K_2SO_4, but a high level of magnesium

($MgSO_4$ weight fraction similar to K_2SO_4) resulted in a mixed sulphate of K and Mg.

In addition, solutions with calcium had disproportionally high calcium levels in crystallised potassium sulphate. It is possible that small amounts of calcium precipitated as gypsum, a compound that has a low solubility. The test samples contained much less calcium than the case process, so the actual feed could have more significant gypsum precipitation. In actual EFC application of a similar process, the possibility of mixed gypsum and primary salt product should be taken into account if calcium is not removed before cooling. All in all, solution components with a good aqueous solubility and low concentration seem not to significantly affect the eutectic crystallisation of K_2SO_4. The sodium-based mine concentrate sample produced similar results in salt purity, with the main difference being eutectic temperature. Sulphates of sodium and potassium appeared technically feasible as EFC products from mine concentrate.

During crystalliser construction and modification, disadvantages of EFC described in the literature were observed. Ice scaling on heat transfer walls was a constant vulnerability and the main reason for several equipment iterations. The phenomenon could not be completely eliminated, and even the last crystalliser iteration required periodic manual ice removal. However, cooling parameters such as mixing and temperature difference between solution and coolant were found to affect the severity of scaling. Additionally, scaling was found to be heaviest when both ice and salt had been crystallised, which is in agreement with some previous studies. Despite difficulties, most scaling was removable manually, which indicates that mechanical scraping could be an effective solution. Non-mechanical solutions might include depositing an ultra-thin layer of hydrophobic material upon the cooling surfaces in contact with the solution.

Economically, the given case process feed may not be profitable due to its dilute nature and the relatively low market value of sodium sulphate. The hypothetical, more concentrated potassium-based feed was found to be promising. Due to its higher market value and anhydrous, relatively high-temperature crystallisation, K_2SO_4 combines a good technical and economic feasibility for EFC production. The hypothetical process was also resistant to increased operational costs, making it less sensitive to possible errors in cost evaluation. A less dilute feed could also be feasible, but due to its eutectic concentration around 8 wt.%, K_2SO_4 benefits more from higher water recovery than sodium sulphate. However, dilute feeds could be compensated with a multi-step EFC process. In addition to salt, ice purity is possible to maintain high as well, contributing to the process.

For further studies on the subject, optimising EFC parameters for maximum crystal and ice quality is recommended. Depending on the specifics of cooling and nucleation, ice and salt crystals were found to have varying sizes and forms, but detailed study of the crystalline structures was beyond the scope of this study. A more accurate and modern evaluation on the capital costs of large-scale EFC systems is also recommended, as high investment is one of the main drawbacks of the method. However, continuation of research and applications are likely to decrease equipment costs in the long run. All in all, EFC seems to be a promising technology for profitable sulphate salt extraction but it requires significant initial investment.

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Appendix I 1/3

Breakdown of price sources

Na_2SO_4, anhydrous, all accessed 19.5.2017

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